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(54) Title: LOW-SULFUR REFORMING PROCESSES			
(57) Abstract			
Disclosed is a method for reforming hydrocarbons comprising contacting the hydrocarbons with a catalyst in a reactor system (10, 20, 30) of improved resistance to carburization and metal dusting under conditions of low sulfur.			

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## 1 LOW-SULFUR REFORMING PROCESSES

2  
3 BACKGROUND OF THE INVENTION

4 This application is a continuation-in-part  
5 application of U.S. Application No. 07/666,696, filed  
6 March 8, 1991, the contents of which is hereby  
7 incorporated by reference, and is related to U.S.  
8 Application No. 802,821 [Attorney's Docket No.  
9 005950-316], and U.S. Application No. 803,215  
10 [Attorney's Docket No. 005950-333], both filed  
11 concurrently herewith and the contents of which are  
12 hereby incorporated by reference.

13  
14 The present invention relates to improved  
15 techniques for catalytic reforming, particularly,  
16 catalytic reforming under low-sulfur, and low-sulfur  
17 and low-water conditions. More specifically, the  
18 invention relates to the discovery and control of  
19 problems particularly acute with low-sulfur, and low-  
20 sulfur and low-water reforming processes.

21 Catalytic reforming is well known in the  
22 petroleum industry and involves the treatment of  
23 naphtha fractions to improve octane rating by the  
24 production of aromatics. The more important  
25 hydrocarbon reactions which occur during the

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1 reforming operation include the dehydrogenation of  
2 cyclohexanes to aromatics, dehydroisomerization of  
3 alkylcyclopentanes to aromatics, and  
4 dehydrocyclization of acyclic hydrocarbons to  
5 aromatics. A number of other reactions also occur,  
6 including the dealkylation of alkylbenzenes,  
7 isomerization of paraffins, and hydrocracking  
8 reactions which produce light gaseous hydrocarbons,  
9 e.g., methane, ethane, propane and butane. It is  
10 important to minimize hydrocracking reactions during  
11 reforming as they decrease the yield of gasoline  
12 boiling products and hydrogen.

13  
14 Because there is a demand for high octane  
15 gasoline, extensive research has been devoted to the  
16 development of improved reforming catalysts and  
17 catalytic reforming processes. Catalysts for  
18 successful reforming processes must possess good  
19 selectivity. That is, they should be effective for  
20 producing high yields of liquid products in the  
21 gasoline boiling range containing large  
22 concentrations of high octane number aromatic  
23 hydrocarbons. Likewise, there should be a low yield  
24 of light gaseous hydrocarbons. The catalysts should  
25 possess good activity to minimize excessively high  
26 temperatures for producing a certain quality of

- 3 -

1 products. It is also necessary for the catalysts to  
2 either possess good stability in order that the  
3 activity and selectivity characteristics can be  
4 retained during prolonged periods of operation; or be  
5 sufficiently regenerable to allow frequent  
6 regeneration without loss of performance.

7

8 Catalytic reforming is also an important process  
9 for the chemical industry. There is an increasingly  
10 larger demand for aromatic hydrocarbons for use in  
11 the manufacture of various chemical products such as  
12 synthetic fibers, insecticides, adhesives,  
13 detergents, plastics, synthetic rubbers,  
14 pharmaceutical products, high octane gasoline,  
15 perfumes, drying oils, ion-exchange resins, and  
16 various other products well known to those skilled in  
17 the art.

18

19 An important technological advance in catalytic  
20 reforming has recently emerged which involves the use  
21 of large-pore zeolite catalysts. These catalysts are  
22 further characterized by the presence of an alkali or  
23 alkaline earth metal and are charged with one or more  
24 Group VIII metals. This type of catalyst has been  
25 found to advantageously provide higher selectivity  
26 and longer catalytic life than those previously used.

- 4 -

1           Having discovered selective catalysts with  
2   acceptable cycle lives, successful commercialization  
3   seemed inevitable. Unfortunately, it was  
4   subsequently discovered that the highly selective,  
5   large pore zeolite catalysts containing a Group VIII  
6   metal were unusually susceptible to sulfur poisoning.  
7   See U.S. Patent No. 4,456,527. Ultimately, it was  
8   found that to effectively address this problem,  
9   sulfur in the hydrocarbon feed should be at ultra-low  
10   levels, preferably less than 100 parts per billion  
11   (ppb), more preferably less than 50 ppb to achieve an  
12   acceptable stability and activity level for the  
13   catalysts.

14  
15           After recognizing the sulfur sensitivity  
16   associated with these new catalysts and determining  
17   the necessary and acceptable levels of process  
18   sulfur, successful commercialization reappeared on  
19   the horizon; only to vanish with the emergence of  
20   another associated problem. It was found that  
21   certain large pore zeolite catalysts are also  
22   adversely sensitive to the presence of water under  
23   typical reaction conditions. Particularly, water was  
24   found to greatly accelerate the rate of catalyst  
25   deactivation.

26

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1       Water sensitivity was found to be a serious  
2       drawback which was difficult to effectively address.  
3       Water is produced at the beginning of each process  
4       cycle when the catalyst is reduced with hydrogen.  
5       And, water can be produced during process upsets when  
6       water leaks into the reformer feed, or when the feed  
7       becomes contaminated with an oxygen-containing  
8       compound. Eventually, technologies were also  
9       developed to protect the catalysts from water.

10

11       Again commercialization seemed practical with  
12       the development of various low-sulfur, low-water  
13       systems for catalytic reforming using highly  
14       selective large-pore zeolite catalysts with long  
15       catalytic lives. While low-sulfur/low-water systems  
16       were initially effective, it was discovered that a  
17       shut down of the reactor system can be necessary  
18       after only a matter of weeks. The reactor system of  
19       one test plant had regularly become plugged after  
20       only such brief operating periods. The plugs were  
21       found to be those associated with coking. However,  
22       although coking within catalyst particles is a common  
23       problem in hydrocarbon processing, the extent and  
24       rate of coke plug formation exterior to the catalyst  
25       particles associated with this particular system far  
26       exceeded any expectation.

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SUMMARY OF THE INVENTION

1

2       Accordingly, one object of the invention is to  
3 provide a method for reforming hydrocarbons under  
4 conditions of low sulfur which avoids the  
5 aforementioned problems found to be associated with  
6 low-sulfur processes, such as brief operating  
7 periods.

8

9       It is another object of the invention to provide  
10 a reactor system for reforming hydrocarbons under  
11 conditions of low sulfur which permits longer  
12 operating periods.

13

14       After a detailed analysis and investigation of  
15 the coke plugs of low-sulfur reactor systems, it was  
16 surprisingly found that they contained particles and  
17 droplets of metal; the droplets ranging in size of up  
18 to a few microns. This observation led to the  
19 startling realization that there are new, profoundly  
20 serious, problems which were not of concern with  
21 conventional reforming techniques where process  
22 sulfur and water levels were significantly higher.  
23 More particularly, it was discovered that problems  
24 existed which threatened the effective and economic  
25 operability of the systems, and the physical  
26 integrity of the equipment as well. It was also



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1 discovered that these problems emerged due to the  
2 low-sulfur conditions, and to some extent, the low  
3 levels of water.  
4

5 For the last forty years, catalytic reforming  
6 reactor systems have been constructed of ordinary  
7 mild steel (e.g., 2½ Cr 1 Mo). Over time, experience  
8 has shown that the systems can operate successfully  
9 for about twenty years without significant loss of  
10 physical strength. However, the discovery of the  
11 metal particles and droplets in the coke plugs  
12 eventually lead to an investigation of the physical  
13 characteristics of the reactor system. Quite  
14 surprisingly, conditions were discovered which are  
15 symptomatic of a potentially severe physical  
16 degradation of the entire reactor system, including  
17 the furnace tubes, piping, reactor walls and other  
18 environments such as catalysts that contain iron and  
19 metal screens in the reactors. Ultimately, it was  
20 discovered that this problem is associated with the  
21 excessive carburization of the steel which causes an  
22 embrittlement of the steel due to injection of  
23 process carbon into the metal. Conceivably, a  
24 catastrophic physical failure of the reactor system  
25 could result.

26

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1 With conventional reforming techniques  
2 carburization simply was not a problem or concern;  
3 nor was it expected to be in contemporary low-  
4 sulfur/low-water systems. And, it was assumed that  
5 conventional process equipment could be used.  
6 Apparently, however, the sulfur present in  
7 conventional systems effectively inhibits  
8 carburization. Somehow in conventional processes the  
9 process sulfur interferes with the carburization  
10 reaction. But with extremely low-sulfur systems,  
11 this inherent protection no longer exists.

12

13 Figure 1A is a photomicrograph of a portion of  
14 the inside (process side) of a mild steel furnace  
15 tube from a commercial reformer. The tube had been  
16 exposed to conventional reforming conditions for  
17 about 19 years. This photograph shows that the  
18 surface of the tube has remained essentially  
19 unaltered with the texture of the tube remaining  
20 normal after long exposure to hydrocarbons at high  
21 temperatures (the black portion of the photograph is  
22 background).

23

24 Figure 1B is a photomicrograph of a portion of a  
25 mild steel coupon sample which was placed inside a  
26 reactor of a low-sulfur/low-water demonstration plant

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1 for only 13 weeks. The photograph shows the eroded  
2 surface of the sample (contrasted against a black  
3 background) from which metal dusting has occurred.  
4 The dark grey-like veins indicate the environmental  
5 carburization of the steel, which was carburized and  
6 embrittled more than 1 mm in depth.

7  
8 Of course, the problems associated with  
9 carburization only begin with carburization of the  
10 physical system. The carburization of the steel  
11 walls leads to "metal dusting"; a release of  
12 catalytically active particles and melt droplets of  
13 metal due to erosion of the metal.

14  
15 The active metal particulates provide additional  
16 sites for coke formation in the system. While  
17 catalyst deactivation from coking is generally a  
18 problem which must be addressed in reforming, this  
19 new significant source of coke formation leads to a  
20 new problem of coke plugs which excessively  
21 aggravates the problem. In fact, it was found that  
22 the mobile active metal particulates and coke  
23 particles metastasize coking generally throughout the  
24 system. The active metal particulates actually  
25 induce coke formation on themselves and anywhere that  
26 the particles accumulate in the system resulting in

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1 coke plugs and hot regions of exothermic  
2 demethanation reactions. As a result, an  
3 unmanageable and premature coke-plugging of the  
4 reactor system occurs which can lead to a system  
5 shut-down within weeks of start-up. Use of the  
6 process and reactor system of the present invention,  
7 however, overcomes these problems.

8  
9 Therefore, a first aspect of the invention  
10 relates to a method for reforming hydrocarbons  
11 comprising contacting the hydrocarbons with a  
12 reforming catalyst, preferably a large-pore zeolite  
13 catalyst including an alkali or alkaline earth metal  
14 and charged with one or more Group VIII metals, in a  
15 reactor system having a resistance to carburization  
16 and metal dusting which is an improvement over  
17 conventional mild steel reactor systems under  
18 conditions of low sulfur and often low sulfur and low  
19 water, and upon reforming the resistance being such  
20 that embrittlement from carburization will be less  
21 than about 2.5 mm/year, preferably less than 1.5  
22 mm/year, more preferably less than 1 mm/year, and  
23 most preferably less than 0.1 mm/year. Preventing  
24 embrittlement to such an extent will significantly  
25 reduce metal dusting and coking in the reactor

- 11 -

1 system, and permits operation for longer periods of  
2 time.

3  
4 And, another aspect of the invention relates to  
5 a reactor system including means for providing a  
6 resistance to carburization and metal dusting which  
7 is an improvement over conventional mild steel  
8 systems in a method for reforming hydrocarbons using  
9 a reforming catalyst such as a large-pore zeolite  
10 catalyst including an alkaline earth metal and  
11 charged with one or more Group VIII metals under  
12 conditions of low sulfur, the resistance being such  
13 that embrittlement will be less than about 2.5  
14 mm/year, preferably less than 1.5 mm/year, more  
15 preferably less than 1 mm/year, and most preferably  
16 less than 0.1 mm/year.

17  
18 Thus, among other factors, the present invention  
19 is based on the discovery that in low-sulfur, and  
20 low-sulfur and low-water reforming processes there  
21 exist significant carburization, metal dusting and  
22 coking problems, which problems do not exist to any  
23 significant extent in conventional reforming  
24 processes where higher levels of sulfur are present.  
25 This discovery has led to intensive work and  
26 development of solutions to the problems, which

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1 solutions are novel to low-sulfur reforming and are  
2 directed to the identification and selection of  
3 resistant materials for low-sulfur reforming systems,  
4 ways to effectively utilize and apply the resistant  
5 materials, additives (other than sulfur) for reducing  
6 carburization, metal dusting and coking, various  
7 process modifications and configurations, and  
8 combinations thereof, which effectively address the  
9 problems.

10

11 More particularly, the discovery has led to the  
12 search for, identification of, and selection of  
13 resistant materials for low-sulfur reforming systems,  
14 preferably the reactor walls, furnace tubes and  
15 screens thereof, which were previously unnecessary in  
16 conventional reforming systems such as certain alloy  
17 and stainless steels, aluminized and chromized  
18 materials, and certain ceramic materials. Also, it  
19 was discovered that other specific materials, applied  
20 as a plating, cladding, paint, etc., can be  
21 effectively resistant. These materials include  
22 copper, tin, arsenic, antimony, brass, lead bismuth  
23 chromium, intermetallic compounds thereof, and alloys  
24 thereof, as well as silica and silicon based  
25 coatings. In one preferred embodiment of the

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1 invention there is provided a novel and resistant  
2 tin-containing paint.  
3

4 Furthermore, the discovery led to the  
5 development of certain additives, hereinafter  
6 referred to as anticarburing and anticoking agents,  
7 which out of necessity are essentially sulfur free,  
8 preferably completely sulfur free, which are novel to  
9 reforming. Such additives include organo-tin  
10 compounds, organo-antimony compounds, organo-bismuth  
11 compounds, organo-arsenic compounds and organo-lead  
12 compounds.  
13

14 Also, the problems associated with low-sulfur  
15 reforming has lead to the development of certain  
16 process modifications and configurations previously  
17 unnecessary in conventional reforming. These include  
18 certain temperature control techniques, the use of  
19 superheated hydrogen between reactors, more frequent  
20 catalyst regenerations, the use of staged heaters and  
21 tubes, the use of staged temperature zones, the use  
22 of superheated raw materials, and the use of larger  
23 tube diameters and/or higher tube velocities.  
24  
25

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BRIEF DESCRIPTION OF THE DRAWING

1  
2 As noted above, Figure 1A is a photomicrograph  
3 of a portion of the inside (process side) of a mild  
4 steel furnace tube from a commercial reformer which  
5 had been in use about 19 years; and as also noted  
6 above,

7  
8 Figure 1B is a photomicrograph of a portion of a  
9 mild steel coupon sample which was placed inside a  
10 reactor of a low-sulfur/low-water demonstration plant  
11 for only 13 weeks.

12  
13 Figure 2 is an illustration of a suitable  
14 reforming reactor system for use in the present  
15 invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

16  
17  
18 The metallurgical terms used herein are to be  
19 given their common metallurgical meanings as set  
20 forth in THE METALS HANDBOOK of the American Society  
21 of Metals. For example, "carbon steels" are those  
22 steels having no specified minimum quantity for any  
23 alloying element (other than the commonly accepted  
24 amounts of manganese, silicon and copper) and  
25 containing only an incidental amount of any element  
26 other than carbon, silicon, manganese, copper, sulfur



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1 and phosphorus. "Mild steels" are those carbon  
2 steels with a maximum of about 0.25% carbon. Alloy  
3 steels are those steels containing specified  
4 quantities of alloying elements (other than carbon  
5 and the commonly accepted amounts of manganese,  
6 copper, silicon, sulfur and phosphorus) within the  
7 limits recognized for constructional alloy steels,  
8 added to effect changes in mechanical or physical  
9 properties. Alloy steels will contain less than 10%  
10 chromium. Stainless steels are any of several steels  
11 containing at least 10, preferably 12 to 30%,  
12 chromium as the principal alloying element.

13

14 Generally, therefore, one focus of the invention  
15 is to provide an improved method for reforming  
16 hydrocarbons using a reforming catalyst, particularly  
17 a large pore zeolite catalyst including an alkali or  
18 alkaline earth metal and charged with one or more  
19 Group VIII metals which is sulfur sensitive, under  
20 conditions of low sulfur. Such a process, of course,  
21 must demonstrate better resistance to carburization  
22 than conventional low-sulfur reforming techniques.

23

24 One solution for the problem addressed by the  
25 present invention is to provide a novel reactor  
26 system which can include one or more various means

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1 for improving resistance to carburization and metal  
2 dusting during reforming using a reforming catalyst  
3 such as the aforementioned sulfur sensitive large-  
4 pore zeolite catalyst under conditions of low sulfur.

5  
6 By "reactor system" as used herein there is  
7 intended at least one reforming reactor and its  
8 corresponding furnace means and piping. Figure 2  
9 illustrates a typical reforming reactor system  
10 suitable for practice of the present invention. It  
11 can include a plurality of reforming reactors (10),  
12 (20) and (30). Each reactor contains a catalyst bed.  
13 The system also includes a plurality of furnaces  
14 (11), (21) and (31); heat exchanger (12); and  
15 separator (13).

16  
17 Through research associated with the present  
18 invention, it was discovered that the aforementioned  
19 problems with low-sulfur reforming can be effectively  
20 addressed by a selection of an appropriate reactor  
21 system material for contact with the hydrocarbons  
22 during processing. Typically, reforming reactor  
23 systems have been constructed of mild steels, or  
24 alloy steels such as typical chromium steels, with  
25 insignificant carburization and dusting. For  
26 example, under conditions of standard reforming,  $2\frac{1}{2}$

- 17 -

1 Cr furnace tubes can last twenty years. However, it  
2 was found that these steels are unsuitable under low-  
3 sulfur reforming conditions. They rapidly become  
4 embrittled by carburization within about one year.  
5 For example, it was found that 2½ Cr 1 Mo steel  
6 carburized and embrittled more than 1 mm/year.

7  
8 Furthermore, it was found that materials  
9 considered under standard metallurgical practice to  
10 be resistant to coking and carburization are not  
11 necessarily resistant under low-sulfur reforming  
12 conditions. For example, nickel-rich alloys such as  
13 Incoloy 800 and 825; Inconel 600; Marcel and Haynes  
14 230, are unacceptable as they exhibit excessive  
15 coking and dusting.

16  
17 However, 300 series stainless steels, preferably  
18 304, 316, 321 and 347, are acceptable as materials  
19 for at least portions of the reactor system according  
20 to the present invention which contact the  
21 hydrocarbons. They have been found to have a  
22 resistance to carburization greater than mild steels  
23 and nickel-rich alloys.

24  
25 Initially it was believed that aluminized  
26 materials such as those sold by Alon Corporation

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1 ("Alonized Steels") would not provide adequate  
2 protection against carburization in the reforming  
3 reactor system and process of the invention. It has  
4 since been discovered, however, that the application  
5 of thin aluminum or alumina films to metal surfaces  
6 of the reforming reactor system, or simply the use of  
7 Alonized Steels during construction, can provide  
8 surfaces which are sufficiently resistant to  
9 carburization and metal dusting under the low-sulfur  
10 reforming conditions. However, such materials are  
11 relatively expensive, and while resistant to  
12 carburization and metal dusting, tend to crack, and  
13 show substantial reductions in tensile strengths.  
14 Cracks expose the underlying base metal rendering it  
15 susceptible to carburization and metal dusting under  
16 low sulfur reforming conditions.

17

18 While aluminized materials have been used to  
19 prevent carburization in ethylene steam cracking  
20 processes, such processes are operated at  
21 significantly higher temperatures than reforming;  
22 temperatures where carburization would be expected.  
23 Carburization and metal dusting simply have not been  
24 problems in prior reforming processes.

25

- 19 -

1       Therefore, another solution to the problems of  
2       carburization and metal dusting involves the  
3       application of thin aluminum or alumina films on, or  
4       the use of aluminized materials as, at least a  
5       portion of the metal surfaces in the reactor system.  
6       In fact, the metal surfaces particularly susceptible  
7       to carburization and metal dusting can be provided in  
8       that manner. Such metal surfaces include but are not  
9       limited to, the reactor walls, furnace tubes, and  
10      furnace liners.

11  
12       When applying an aluminum or alumina film, it is  
13      preferable that the film have a thermal expansivity  
14      that is similar to that of the metal surface to which  
15      it is applied (such as a mild steel) in order to  
16      withstand thermal shocks and repeated temperature  
17      cycling which occur during reforming. This prevents  
18      cracking or spalling of the film which could expose  
19      the underlying metal surface to the carburization  
20      inducing hydrocarbon environment.

21  
22       Additionally, the film should have a thermal  
23      conductivity similar to that of, or exceeding, those  
24      of metals conventionally used in the construction of  
25      reforming reactor systems. Furthermore, the aluminum  
26      or alumina film should not degrade in the reforming

- 20 -

1 environment, or in the oxidizing environment  
2 associated with catalyst regeneration, nor should it  
3 result in the degradation of the hydrocarbons in the  
4 reactor system.

5  
6       Suitable methods for applying aluminum or  
7 alumina films to metal surfaces such as mild steels  
8 include well known deposition techniques. Preferred  
9 processes include powder and vapor diffusion  
10 processes such as the "Alonizing" process, which has  
11 been commercialized by Alon Processing, Inc.,  
12 Terrytown, Pa.

13  
14       Essentially, "Alonizing" is a high temperature  
15 diffusion process which alloys aluminum into the  
16 surface of a treated metal, such as e.g., a  
17 commercial grade mild steel. In this process, the  
18 metal (e.g., a mild steel) is positioned in a retort  
19 and surrounded with a mixture of blended aluminum  
20 powders. The retort is then hermetically sealed and  
21 placed in an atmosphere-controlled furnace. At  
22 elevated temperatures, the aluminum deeply diffuses  
23 into the treated metal resulting in an alloy. After  
24 furnace cooling, the substrate is taken out of the  
25 retort and excess powder is removed. Straightening,  
26 trimming, beveling and other secondary operations can

- 21 -

1 then be performed as required. This process can  
2 render the treated ("alozized") metal resistant to  
3 carburization and metal dusting under low-sulfur  
4 reforming conditions according to the invention.

5  
6 Thin chromium or chromium oxide films can also  
7 be applied to metal surfaces of the reactor system to  
8 render the surfaces resistant to carburization and  
9 metal dusting under low-sulfur reforming conditions.  
10 Like the use of alumina and aluminum films, and  
11 aluminized materials, chromium or chromium oxide  
12 coated metal surfaces have not been used to address  
13 carburization problems under low-sulfur reforming  
14 conditions.

15  
16 The chromium or chromium oxide can also be  
17 applied to carburization and metal dusting  
18 susceptible metal surfaces such as the reactor walls,  
19 furnace liners, and furnace tubes. However, any  
20 surface in the system which would show signs of  
21 carburization and metal dusting under low-sulfur  
22 reforming conditions would benefit from the  
23 application of a thin chromium or chromium oxide  
24 film.

25

- 22 -

1       When applying the chromium or chromium oxide  
2 film, it is preferable that the chromium or chromium  
3 oxide film have a thermal expansivity similar to that  
4 of the metal to which it is applied. Additionally,  
5 the chromium or chromium oxide film should be able to  
6 withstand thermal shocks and repeated temperature  
7 cycling which are common during reforming. This  
8 avoids cracking or spalling of the chromium or  
9 chromium oxide film which could potentially expose  
10 the underlying metal surfaces to carburization  
11 inducing environments. Furthermore, the chromium or  
12 chromium oxide film should have a thermal  
13 conductivity similar to or exceeding those materials  
14 conventionally used in reforming reactor systems (in  
15 particular mild steels) in order to maintain  
16 efficient heat transfer. The chromium or chromium  
17 oxide film also should not degrade in the reforming  
18 environment or in the oxidizing environment  
19 associated with catalyst regeneration, nor should it  
20 induce degradation of the hydrocarbons in the reactor  
21 system.

22  
23       Suitable methods for applying chromium or  
24 chromium oxide films to surfaces such as e.g., mild  
25 steels, include well known deposition techniques.  
26 Preferred processes include powder-pack and vapor



- 23 -

1 diffusion processes such as the "chromizing" process,  
2 which is commercialized by Alloy Surfaces, Inc., of  
3 Wilmington, Delaware.

4  
5 The "chromizing" process is essentially a vapor  
6 diffusion process for application of chromium to a  
7 metal surface (similar to the above described  
8 "Alonizing process"). The process involves  
9 contacting the metal to be coated with a powder of  
10 chromium, followed by a thermal diffusion step.  
11 This, in effect, creates an alloy of the chromium  
12 with the treated metal and renders the surface  
13 extremely resistant to carburization and metal  
14 dusting under low-sulfur reforming conditions.

15  
16 In some areas of the reactor systems, localized  
17 temperatures can become excessively high during  
18 reforming (e.g., 900-1250°F). This is particularly  
19 the case in furnace tubes, and in catalyst beds where  
20 exothermic demethanation reactions occur within  
21 normally occurring coke balls causing localized hot  
22 regions. While still preferred to mild steels and  
23 nickel-rich alloys, the 300 series stainless steels  
24 do exhibit some coking and dusting at around 1000°F.  
25 Thus, while useful, the 300 series stainless steels

- 24 -

1 are not the most preferred material for use in the  
2 present invention.

3

4 Chromium-rich stainless steels such as 446 and  
5 430 are even more resistant to carburization than 300  
6 series stainless steels. However, these steels are  
7 not as desirable for heat resisting properties (they  
8 tend to become brittle).

9

10 Resistant materials which are preferred over the  
11 300 series stainless steels for use in the present  
12 invention include copper, tin, arsenic, antimony,  
13 bismuth, chromium and brass, and intermetallic  
14 compounds and alloys thereof (e.g., Cu-Sn alloys, Cu-  
15 Sb alloys, stannides, antimonides, bismuthides,  
16 etc.). Steels and even nickel-rich alloys containing  
17 these metals can also show reduced carburization. In  
18 a preferred embodiment, these materials are provided  
19 as a plating, cladding, paint (e.g., oxide paints) or  
20 other coating to a base construction material. This  
21 is particularly advantageous since conventional  
22 construction materials such as mild steels can still  
23 be used with only the surface contacting the  
24 hydrocarbons being treated. Of these, tin is  
25 especially preferred as it reacts with the surface to  
26 provide a coating having excellent carburization

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1 resistance at higher temperatures, and which resists  
2 peeling and flaking of the coating. Also, it is  
3 believed that a tin containing layer can be as thin  
4 as 1/10 micron and still prevent carburization.

5  
6 Where practical, it is preferred that the  
7 resistant materials be applied in a paint-like  
8 formulation (hereinafter "paint") to a new or  
9 existing reactor system. Such a paint can be  
10 sprayed, brushed, pigged, etc. on reactor system  
11 surfaces such as mild steels or stainless steels. It  
12 is most preferred that such a paint be a  
13 decomposable, reactive, tin-containing paint which  
14 reduces to a reactive tin and forms metallic  
15 stannides (e.g., iron stannides and nickel/iron  
16 stannides) upon heating in a reducing atmosphere.

17  
18 It is most preferred that the aforementioned  
19 paint contain at least four components (or their  
20 functional equivalents); (i) a hydrogen decomposable  
21 tin compound, (ii) a solvent system, (iii) a finely  
22 divided tin metal and (iv) tin oxide as a reducible  
23 sponge/dispersing/binding agent. The paint should  
24 contain finely divided solids to minimize settling,  
25 and should not contain non-reactive materials which

- 26 -

1 will prevent reaction of reactive tin with surfaces  
2 of the reactor system.

3  
4 As the hydrogen decomposable tin compound, tin  
5 octanoate is particularly useful. Commercial  
6 formulations of this compound itself are available  
7 and will partially dry to an almost chewing-gum-like  
8 layer on a steel surface; a layer which will not  
9 crack and/or split. This property is necessary for  
10 any coating composition used in this context because  
11 it is conceivable that the coated material will be  
12 stored for months prior to treatment with hydrogen.  
13 Also, if parts are coated prior to assembly they must  
14 be resistant to chipping during construction. As  
15 noted above, tin octanoate is available commercially.  
16 It is reasonably priced, and will decompose smoothly  
17 to a reactive tin layer which forms iron stannide in  
18 hydrogen at temperatures as low as 600°F.

19  
20 Tin octanoate should not be used alone in a  
21 paint, however. It is not sufficiently viscous.  
22 Even when the solvent is evaporated therefrom, the  
23 remaining liquid will drip and run on the coated  
24 surface. In practice, for example, if such were used  
25 to coat a horizontal furnace tube, it would pool at  
26 the bottom of the tube.

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1           Component (iv), the tin oxide  
2    sponge/dispersing/binding agent, is a porous tin-  
3    containing compound which can sponge-up an organo-  
4    metallic tin compound, yet still be reduced to active  
5    tin in the reducing atmosphere. In addition, tin  
6    oxide can be processed through a colloid mill to  
7    produce very fine particles which resist rapid  
8    settling. The addition of tin oxide will provide a  
9    paint which becomes dry to the touch, and resists  
10   running.

11  
12           Unlike typical paint thickeners, component (iv)  
13   is selected such that it becomes a reactive part of  
14   the coating when reduced. It is not inert like  
15   formed silica; a typical paint thickener which would  
16   leave an unreactive surface coating after treatment.

17  
18           Finely divided tin metal, component (iii), is  
19   added to insure that metallic tin is available to  
20   react with the surface to be coated at as low a  
21   temperature as possible, even in a non-reducing  
22   atmosphere. The particle size of the tin is  
23   preferably one to five microns which allows excellent  
24   coverage of the surface to be coated with tin metal.  
25   Non-reducing conditions can occur during drying of  
26   the paint and welding of pipe joints. The presence

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1 of metallic tin ensures that even when part of the  
2 coating is not completely reduced, tin metal will be  
3 present to react and form the desired stannide layer.

4  
5 The solvent should be non-toxic, and effective  
6 for rendering the paint sprayable and spreadable when  
7 desired. It should also evaporate quickly and have  
8 compatible solvent properties for the hydrogen  
9 decomposable tin compound. Isopropyl alcohol is most  
10 preferred, while hexane and pentane can be useful, if  
11 necessary. Acetone, however, tends to precipitate  
12 organic tin compounds.

13  
14 In one embodiment, there can be used a tin paint  
15 of 20 percent Tin Ten-Cem (stannous octanoate in  
16 octanoic acid), stannic oxide, tin metal powder and  
17 isopropyl alcohol.

18  
19 The tin paint can be applied in many ways. For  
20 example, furnace tubes of the reactor system can be  
21 painted individually or as modules. A reforming  
22 reactor system according to the present invention can  
23 contain various numbers of furnace tube modules  
24 (e.g., about 24 furnace tube modules) of suitable  
25 width, length and height (e.g., about 10 feet long,  
26 about 4 feet wide, and about 40 feet in height).

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1 Typically, each module will include two headers of  
2 suitable diameter, preferably about 2 feet in  
3 diameter, which are connected by about four to ten u-  
4 tubes of suitable length (e.g., about 42 feet long).  
5 Therefore, the total surface area to be painted in  
6 the modules can vary widely; for example, in one  
7 embodiment it can be about 16,500 ft<sup>2</sup>.

8  
9       Painting modules rather than the tubes  
10 individually can be advantageous in at least four  
11 respects; (i) painting modules rather than individual  
12 tubes should avoid heat destruction of the tin paint  
13 as the components of the modules are usually heat  
14 treated at extremely elevated temperatures during  
15 production; (ii) painting modules will likely be  
16 quicker and less expensive than painting tubes  
17 individually; (iii) painting modules should be more  
18 efficient during production scheduling; and (iv)  
19 painting of the modules should enable painting of  
20 welds.

21  
22       However, painting the modules may not enable the  
23 tubes to be as completely coated with paint as if the  
24 tubes were painted individually. If coating is  
25 insufficient, the tubes can be coated individually.

26

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1       It is preferable that the paint be sprayed into  
2       the tubes and headers. Sufficient paint should be  
3       applied to fully coat the tubes and headers. After a  
4       module is sprayed, it should be left to dry for about  
5       24 hours followed by application of a slow stream of  
6       heated nitrogen (e.g., about 150°F for about 24  
7       hours). Thereafter, it is preferable that a second  
8       coat of paint be applied and also dried by the  
9       procedure described above. After the paint has been  
10      applied, the modules should preferably be kept under  
11      a slight nitrogen pressure and should not be exposed  
12      to temperatures exceeding about 200°F prior to  
13      installation, nor should they be exposed to water  
14      except during hydrotesting.

15

16       Iron bearing reactive paints are also useful in  
17      the present invention. Such an iron bearing reactive  
18      paint will preferably contain various tin compounds  
19      to which iron has been added in amounts up to one  
20      third Fe/Sn by weight.

21

22       The addition of iron can, for example, be in the  
23      form of  $\text{Fe}_2\text{O}_3$ . The addition of iron to a tin  
24      containing paint should afford noteworthy advantages;  
25      in particular: (i) it should facilitate the  
26      reaction of the paint to form iron stannides thereby



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1 acting as a flux; (ii) it should dilute the nickel  
2 concentration in the stannide layer thereby providing  
3 better protection against coking; and (iii) it  
4 should result in a paint which affords the anti-  
5 coking protection of iron stannides even if the  
6 underlying surface does not react well.

7  
8 Yet another means for preventing carburization,  
9 coking, and metal dusting in the low-sulfur reactor  
10 system comprises the application of a metal coating  
11 or cladding to chromium rich steels contained in the  
12 reactor system. These metal coatings or claddings  
13 may be comprised of tin, antimony, bismuth or  
14 arsenic. Tin is especially preferred. These  
15 coatings or claddings may be applied by methods  
16 including electroplating, vapor depositing, and  
17 soaking of the chromium rich steel in a molten metal  
18 bath.

19  
20 It has been found that in reforming reactor  
21 systems where carburization, coking, and metal  
22 dusting are particularly problematic that the coating  
23 of the chromium-rich, nickel-containing steels with a  
24 layer of tin in effect creates a double protective  
25 layer. There results an inner chromium rich layer  
26 which is resistant to carburization, coking, and

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1 metal dusting and an outer tin layer which is also  
2 resistant to carburization, coking and metal dusting.  
3 This occurs because when the tin coated chromium rich  
4 steel is exposed to typical reforming temperatures,  
5 such as about 1200°F, it reacts with the steel to  
6 form iron nickel stannides. Thereby, the nickel is  
7 preferentially leached from the surface of the steel  
8 leaving behind a layer of chromium rich steel. In  
9 some instances, it may be desirable to remove the  
10 iron nickel stannide layer from the stainless steel  
11 to expose the chromium rich steel layer.

12

13 For example, it was found that when a tin  
14 cladding was applied to a 304 grade stainless steel  
15 and heated at about 1200°F there resulted a chromium  
16 rich steel layer containing about 17% chromium and  
17 substantially no nickel, comparable to 430 grade  
18 stainless steel.

19

20 When applying the tin metal coating or cladding  
21 to the chromium rich steel, it may be desirable to  
22 vary the thickness of the metal coating or cladding  
23 to achieve the desired resistance against  
24 carburization, coking, and metal dusting. This can  
25 be done by, e.g., adjusting the amount of time the  
26 chromium rich steel is soaked in a molten tin bath.

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1 This will also affect the thickness of the resulting  
2 chromium rich steel layer. It may also be desirable  
3 to vary the operating temperature, or to vary the  
4 composition of the chromium rich steel which is  
5 coated which in order to control the chromium  
6 concentration in the chromium rich steel layer  
7 produced.

8  
9 It has additionally been found that tin-coated  
10 steels can be further protected from carburization,  
11 metal dusting, and coking by a post-treatment process  
12 which involves application of a thin oxide coating,  
13 preferably a chromium oxide, such as  $\text{Cr}_2\text{O}_3$ . This  
14 coating will be thin, as thin as a few  $\mu\text{m}$ .  
15 Application of such a chromium oxide will protect  
16 aluminum as well as tin coated steels, such as  
17 Alonized steels, under low-sulfur reforming  
18 conditions.

19  
20 The chromium oxide layer can be applied by  
21 various methods including: application of a chromate  
22 or dichromate paint followed by a reduction process;  
23 vapor treatment with an organo-chromium compound; or  
24 application of a chromium metal plating followed by  
25 oxidation of the resulting chromium plated steel.

26

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1       Examination of tin-electroplated steels which  
2       have been subjected to low-sulfur reforming  
3       conditions for a substantial period of time has shown  
4       that when a chromium oxide layer is produced on the  
5       surface of the stannide layer or under the stannide  
6       layer, the chromium oxide layer does not cause  
7       deterioration of the stannide layer, but appears to  
8       render the steel further resistant to carburization,  
9       coking and metal dusting. Accordingly, application  
10      of a chromium oxide layer to either tin or aluminum  
11      coated steels will result in steels which are further  
12      resistant to carburization and coking under the low-  
13      sulfur reforming conditions. This post-treatment  
14      process has particular applications for treating tin  
15      or aluminum coated steels which, after prolonged  
16      exposure to low-sulfur reforming conditions, are in  
17      need of repair.

18  
19       It has further been found that aluminized, e.g.,  
20      "Alonized" steels which are resistant to  
21      carburization under the present reforming conditions  
22      of low sulfur can be rendered further resistant by  
23      post-treatment of the aluminum coated steel with a  
24      coating of tin. This results in a steel which is  
25      more carburization resistant since there are  
26      cumulative effects of carburization resistance

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1 obtained from both the aluminum coating and the tin  
2 coating. This post-treatment affords an additional  
3 benefit in that it will mend any defects or cracks in  
4 the aluminum, e.g., Alonized, coating. Also, such a  
5 post-treatment should result in a lower cost since a  
6 thinner aluminum coating can be applied to the steel  
7 surface which is to be post-treated with the tin  
8 coating. Additionally, this post-treatment will  
9 protect the underlying steel layer exposed by bending  
10 of aluminized steels, which can introduce cracks in  
11 the aluminum layer, and expose the steel to  
12 carburization induced under reforming conditions.  
13 Also, this post-treatment process can prevent coke  
14 formation on the treated steel surfaces and also  
15 prevent coke formation that occurs on the bottom of  
16 cracks which appear on steels which have been  
17 aluminized, but not additionally coated with tin.

18  
19 Samples of Alonized Steels painted on one side  
20 with tin, were found to show a deposit of black coke  
21 only on the untreated side under low-sulfur reforming  
22 conditions. The coke that forms on an aluminized  
23 surface is a benign coke resulting from cracking on  
24 acidic alumina sites. It is incapable of inducing  
25 additional coke deposition. Accordingly, a post-  
26 treatment application of a tin coating to aluminized

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1 steels can provide further minimization of the  
2 problems of carburization, coking, and metal dusting,  
3 in reactor systems operating under reforming  
4 conditions according to the invention.

5  
6 While not wishing to be bound by theory, it is  
7 believed that the suitability of various materials  
8 for the present invention can be selected and  
9 classified according to their responses to  
10 carburizing atmospheres. For example, iron, cobalt,  
11 and nickel form relatively unstable carbides which  
12 will subsequently carburize, coke and dust. Elements  
13 such as chromium, niobium, vanadium, tungsten,  
14 molybdenum, tantalum and zirconium, will form stable  
15 carbides which are more resistant to carburization  
16 coking and dusting. Elements such as tin, antimony  
17 and bismuth do not form carbides or coke. And, these  
18 compounds can form stable compounds with many metals  
19 such as iron, nickel and copper under reforming  
20 conditions. Stannides, antimonides and bismuthides,  
21 and compounds of lead, mercury, arsenic, germanium,  
22 indium, tellurium, selenium, thallium, sulfur and  
23 oxygen are also resistant. A final category of  
24 materials include elements such as silver, copper,  
25 gold, platinum and refractory oxides such as silica  
26 and alumina. These materials are resistant and do

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1 not form carbides, or react with other metals in a  
2 carburizing environment under reforming conditions.

3  
4 As discussed above, the selection of appropriate  
5 metals which are resistant to carburization and metal  
6 dusting, and their use as coating materials for metal  
7 surfaces in the reactor system is one means for  
8 preventing the carburization and metal dusting  
9 problem. However, carburization and metal dusting  
10 can be prevalent in a wide variety of metals; and  
11 carburization resistant metals can be more costly or  
12 exotic than conventional materials (e.g., mild  
13 steels) used in the construction of reforming reactor  
14 systems. Accordingly, it may be desirable in the  
15 reactor system of the invention to use ceramic  
16 materials which do not form carbides at typical  
17 reforming conditions, and thus are not susceptible to  
18 carburization, for at least a portion of the metal  
19 surfaces in the reactor system. For example, at  
20 least a portion of the furnace tubes, or furnace  
21 liners or both may be constructed of ceramic  
22 materials.

23

24 In choosing the ceramic materials for use in the  
25 present invention, it is preferable that the ceramic  
26 material have thermal conductivities about that or

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1 exceeding those of materials conventionally used in  
2 the construction of reforming reactor systems.  
3 Additionally, the ceramic materials should have  
4 sufficient structural strengths at the temperatures  
5 which occur within the reforming reactor system.  
6 Further, the ceramic materials should be able to  
7 withstand thermal shocks and repeated temperature  
8 cycling which occur during operation of the reactor  
9 system. When the ceramic materials are used for  
10 constructing the furnace liners, the ceramic  
11 materials should have thermal expansivities about  
12 that of the metal outer surfaces with which the liner  
13 is in intimate contact. This avoids undue stress at  
14 the juncture during temperature cycling that occurs  
15 during start-up and shut-down. Additionally, the  
16 ceramic surface should not be susceptible to  
17 degradation in the hydrocarbon environment or in the  
18 oxidizing environment which occurs during catalyst  
19 regeneration. The selected ceramic material also  
20 should not promote the degradation of the  
21 hydrocarbons in the reactor system.

22

23         Suitable ceramic materials include, but are not  
24 restricted to, materials such as silicon carbides,  
25 silicon oxides, silicon nitrides and aluminum  
26 nitrides. Of these, silicon carbides and silicon



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1    nitrides are particularly preferred as they appear  
2    capable of providing complete protection for the  
3    reactor system under low-sulfur reforming conditions.

4  
5        At least a portion of the metal surfaces in the  
6    reactor system can also be coated with a silicon or  
7    silica film. In particular, the metal surfaces which  
8    can be coated include, but are not limited to the  
9    reactor walls, furnace tubes, and furnace liners.  
10   However, any metal surface in the reactor system,  
11   which shows signs of carburization and metal dusting  
12   under low-sulfur reforming conditions would benefit  
13   from the application of a thin silicon or silica  
14   film.

15  
16        Conventional methods can be used for applying  
17    silicon or silica films to coat metal surfaces.  
18    Silica or silicon can be applied by electroplating  
19    and chemical vapor deposition of an alkoxysilane in a  
20    steam carrier gas. It is preferable that the silicon  
21    or silica film have a thermal expansivity about that  
22    of the metal surface which it coats. Additionally,  
23    the silicon or silica film should be able to  
24    withstand thermal shocks and repeated temperature  
25    cycling that occur during reforming. This avoids  
26    cracking or spalling of the silicon or silica film,

- 40 -

1 and potential exposure of the underlying metal  
2 surface to the carburization inducing hydrocarbon  
3 environment. Also, the silica or silicon film should  
4 have a thermal conductivity approximate to or  
5 exceeding that of metals conventionally used in  
6 reforming reactor systems so as to maintain efficient  
7 heat transfer. The silicon or silica film also  
8 should not degrade in the reforming environment or in  
9 the oxidizing environment associated with catalyst  
10 regeneration; nor should it cause degradation of the  
11 hydrocarbons themselves.

12

13 Because different areas of the reactor system of  
14 the invention (e.g., different areas in a furnace)  
15 can be exposed to a wide range of temperatures, the  
16 material selection can be staged, such that those  
17 materials providing better carburization resistances  
18 are used in those areas of the system experiencing  
19 the highest temperatures.

20

21 With regard to materials selection, it was  
22 discovered that oxidized Group VIII metal surfaces  
23 such as iron, nickel and cobalt are more active in  
24 terms of coking and carburization than their  
25 unoxidized counterparts. For example, it was found  
26 that an air roasted sample of 347 stainless steel was

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1 significantly more active than an unoxidized sample  
2 of the same steel. This is believed to be due to a  
3 re-reduction of oxidized steels which produces very  
4 fine-grained iron and/or nickel metals. Such metals  
5 are especially active for carburization and coking.  
6 Thus, it is desirable to avoid these materials as  
7 much as possible during oxidative regeneration  
8 processes, such as those typically used in catalytic  
9 reforming. However, it has been found that an air  
10 roasted 300 series stainless steel coated with tin  
11 can provide similar resistances to coking and  
12 carburization as unroasted samples of the same tin  
13 coated 300 series stainless steel.

14

15 Furthermore, it will be appreciated that  
16 oxidation will be a problem in systems where sulfur  
17 sensitivity of the catalyst is not of concern, and  
18 sulfur is used to passivate the metal surfaces. If  
19 sulfur levels in such systems ever become  
20 insufficient, any metal sulfides which have formed on  
21 metal surfaces would, after oxidation and reduction,  
22 be reduced to fine-grained metal. This metal would  
23 be highly reactive for coking and carburization.  
24 Potentially, this can cause a catastrophic failure of  
25 the metallurgy, or a major coking event.

26

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1       As noted above, excessively high temperatures  
2       can occur in the catalyst beds when exothermic  
3       demethanation reactions within cokeballs cause  
4       localized hot regions. These hot spots also pose a  
5       problem in conventional reforming reactor systems (as  
6       well as other areas of chemical and petrochemical  
7       processing).

8  
9       For example, the center pipe screens of  
10      reformers have been observed to locally waste away  
11      and develop holes; ultimately resulting in catalyst  
12      migration. In conventional reforming processes the  
13      temperatures within cokeballs during formation and  
14      burning are apparently high enough to overcome the  
15      ability of process sulfur to poison coking,  
16      carburization, and dusting. The metal screens,  
17      therefore, carburize and are more sensitive to  
18      wasting by intergranular oxidation (a type of  
19      corrosion) during regeneration. The screen openings  
20      enlarge and holes develop.

21  
22      Thus, the teachings of the present invention are  
23      applicable to conventional reforming, as well as  
24      other areas of chemical and petrochemical processing.  
25      For example, the aforementioned platings, claddings  
26      and coatings can be used in the preparation of center

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1 pipe screens to avoid excessive hole development and  
2 catalyst migration. In addition, the teachings can  
3 be applied to any furnace tubes which are subjected  
4 to carburization, coking and metal dusting, such as  
5 furnace tubes in coker furnaces.

6  
7 In addition, since the techniques described  
8 herein can be used to control carburization, coking,  
9 and metal dusting at excessively high temperatures,  
10 they can be used in cracking furnaces operating at  
11 from about 1400° to about 1700°F. For example, the  
12 deterioration of steel occurring in cracking furnaces  
13 operating at those temperatures can be controlled by  
14 application of various metal coatings. These metal  
15 coatings can be applied by melting, electroplating,  
16 and painting. Painting is particularly preferred.

17  
18 For example, a coating of antimony applied to  
19 iron bearing steels protects these steels from  
20 carburization, coking and metal dusting under the  
21 described cracking conditions. In fact, an antimony  
22 paint applied to iron bearing steels will provide  
23 protection against carburization, coking, and metal  
24 dusting at 1600°F.

25

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1           A coating of bismuth applied to nickel rich  
2   steel alloys (e.g., INCONEL 600) can protect those  
3   steels against carburization, coking, and metal  
4   dusting under cracking conditions. This has been  
5   demonstrated at temperatures of up to 1600°F.

6  
7           Bismuth coatings may also be applied to iron  
8   bearing steels and provide protection against  
9   carburization, metal dusting, and coking under  
10   cracking conditions. Also, a metal coating  
11   comprising a combination of bismuth, antimony, and/or  
12   tin can be used.

13  
14          Looking again to low-sulfur reforming, other  
15   techniques can also be used to address the problem  
16   discovered according to the present invention. They  
17   can be used in conjunction with an appropriate  
18   material selection for the reactor system, or they  
19   can be used alone. Preferred from among the  
20   additional techniques is the addition of non-sulfur,  
21   anti-carburizing and anti-coking agent(s) during the  
22   reforming process. These agents can be added  
23   continuously during processing and function to  
24   interact with those surfaces of the reactor system  
25   which contact the hydrocarbons, or they may be  
26   applied as a pretreatment to the reactor system.

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1        While not wishing to bound by theory it is  
2        believed that these agents interact with the surfaces  
3        of the reactor system by decomposition and surface  
4        attack to form iron and/or nickel intermetallic  
5        compounds, such as stannides, antimonides,  
6        bismuthides, plumbides, arsenides, etc. Such  
7        intermetallic compounds are resistant to  
8        carburization, coking and dusting and can protect the  
9        underlying metallurgy.

10

11       The intermetallic compounds are also believed to  
12       be more stable than the metal sulfides which were  
13       formed in systems where  $H_2S$  was used to passivate the  
14       metal. These compounds are not reduced by hydrogen  
15       as are metal sulfides. As a result, they are less  
16       likely to leave the system than metal sulfides.  
17       Therefore, the continuous addition of a carburization  
18       inhibitor with the feed can be minimized.

19

20       Preferred non-sulfur anti-carburizing and anti-  
21       coking agents include organo-metallic compounds such  
22       as organo-tin compounds, organo-antimony compounds,  
23       organo-bismuth compounds, organo-arsenic compounds,  
24       and organo-lead compounds. Suitable organo-lead  
25       compounds include tetraethyl and tetramethyl lead.

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1    Organo-tin compounds such as tetrabutyl tin and  
2    trimethyl tin hydride are especially preferred.

3

4            Additional specific organo-metallic compounds  
5    include bismuth neodecanoate, chromium octoate,  
6    copper naphthenate, manganese carboxylate, palladium  
7    neodecanoate, silver neodecanoate,  
8    tetrabutylgermanium, tributylantimony,  
9    triphenylantimony, triphenylarsine, and zirconium  
10   octoate.

11

12           How and where these agents are added to the  
13   reactor system is not critical, and will primarily  
14   depend on particular process design characteristics.  
15   For example, they can be added continuously or  
16   discontinuously with the feed.

17

18           However, adding the agents to the feed is not  
19   preferred as they would tend to accumulate in the  
20   initial portions of the reactor system. This may not  
21   provide adequate protection in the other areas of the  
22   system.

23

24           It is preferred that the agents be provided as a  
25   coating prior to construction, prior to start-up, or  
26   in-situ (i.e., in an existing system). If added in-



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1   situ, it should be done right after catalyst  
2   regeneration. Very thin coatings can be applied.  
3   For example, it is believed that when using organo-  
4   tin compounds, iron stannide coatings as thin as 0.1  
5   micron can be effective.

6  
7       A preferred method of coating the agents on an  
8   existing or new reactor surface, or a new or existing  
9   furnace tube is to decompose an organometallic  
10   compound in a hydrogen atmosphere at temperatures of  
11   about 900°F. For organo-tin compounds, for example,  
12   this produces reactive metallic tin on the tube  
13   surface. At these temperatures the tin will further  
14   react with the surface metal to passivate it.

15  
16       Optimum coating temperatures will depend on the  
17   particular organometallic compound, or the mixtures  
18   of compounds if alloys are desired. Typically, an  
19   excess of the organometallic coating agent can be  
20   pulsed into the tubes at a high hydrogen flow rate so  
21   as to carry the coating agent throughout the system  
22   in a mist. The flow rate can then be reduced to  
23   permit the coating metal mist to coat and react with  
24   the furnace tube or reactor surface. Alternatively,  
25   the compound can be introduced as a vapor which

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1 decomposes and reacts with the hot walls of the tube  
2 or reactor in a reducing atmosphere.

3  
4 As discussed above, reforming reactor systems  
5 susceptible to carburization, metal dusting and  
6 coking can be treated by application of a  
7 decomposable coating containing a decomposable  
8 organometallic tin compound to those areas of the  
9 reactor system most susceptible to carburization.  
10 Such an approach works particularly well in a  
11 temperature controlled furnace.

12  
13 However, such control is not always present.  
14 There are "hot spots" which develop in the reactor  
15 system, particularly in the furnace tubes, where the  
16 organometallic compound can decompose and form  
17 deposits. Therefore, another aspect of the invention  
18 is a process which avoids such deposition in  
19 reforming reactor systems where temperatures are not  
20 closely controlled and exhibit areas of high  
21 temperature hot spots.

22  
23 Such a process involves preheating the entire  
24 reactor system to a temperature of from 750 to 1150,  
25 preferably 900 to 1100, and most preferably about  
26 1050°F, with a hot stream of hydrogen gas. After

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1 preheating, a colder gas stream at a temperature of  
2 400 to 800, preferably 500 to 700, and most  
3 preferably about 550°F, containing a vaporized  
4 organometallic tin compound and hydrogen gas is  
5 introduced into the preheated reactor system. This  
6 gas mixture is introduced upstream and can provide a  
7 decomposition "wave" which travels throughout the  
8 entire reactor system.

9

10 Essentially this process works because the hot  
11 hydrogen gas produces a uniformly heated surface  
12 which will decompose the colder organometallic gas as  
13 it travels as a wave throughout the reactor system.  
14 The colder gas containing the organometallic tin  
15 compound will decompose on the hot surface and coat  
16 the surface. The organometallic tin vapor will  
17 continue to move as a wave to treat the hotter  
18 surfaces downstream in the reactor system. Thereby,  
19 the entire reactor system can have a uniform coating  
20 of the organometallic tin compound. It may also be  
21 desirable to conduct several of these hot-cold  
22 temperature cycles to ensure that the entire reactor  
23 system has been uniformly coated with the  
24 organometallic tin compound.

25

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1           In operation of the reforming reactor system  
2   according to the present invention, naphtha will be  
3   reformed to form aromatics. The naphtha feed is a  
4   light hydrocarbon, preferably boiling in the range of  
5   about 70°F to 450°F, more preferably about 100 to  
6   350°F. The naphtha feed will contain aliphatic or  
7   paraffinic hydrocarbons. These aliphatics are  
8   converted, at least in part, to aromatics in the  
9   reforming reaction zone.

10

11           In the "low-sulfur" system of the invention, the  
12   feed will preferably contain less than 100 ppb  
13   sulfur, and more preferably, less than 50 ppb sulfur.  
14   If necessary, a sulfur sorber unit can be employed to  
15   remove small excesses of sulfur.

16

17           Preferred reforming process conditions include a  
18   temperature between 700 and 1050°F, more preferably  
19   between 850 and 1025°F; and a pressure between 0 and  
20   400 psig, more preferably between 15 and 150 psig; a  
21   recycle hydrogen rate sufficient to yield a hydrogen  
22   to hydrocarbon mole ratio for the feed to the  
23   reforming reaction zone between 0.1 and 20, more  
24   preferably between 0.5 and 10; and a liquid hourly  
25   space velocity for the hydrocarbon feed over the

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1 reforming catalyst of between 0.1 and 10, more  
2 preferably between 0.5 and 5.

3

4 To achieve the suitable reformer temperatures,  
5 it is often necessary to heat the furnace tubes to  
6 high temperatures. These temperatures can often  
7 range from 600 to 1800°F, usually from 850 and  
8 1250°F, and more often from 900 and 1200°F.

9

10 As noted above, the problems of carburization,  
11 coking and metal dusting in low-sulfur systems have  
12 been found to associated with excessively high,  
13 localized process temperatures of the reactor system,  
14 and are particularly acute in the furnace tubes of  
15 the system where particularly high temperatures are  
16 characteristic. In conventional reforming techniques  
17 where high levels of sulfur are present, furnace tube  
18 skin temperatures of up to 1175°F at end of run are  
19 typical. Yet, excessive carburization, coking and  
20 metal dusting was not observed. In low-sulfur  
21 systems, however, it has been discovered that  
22 excessive and rapid carburization, coking and metal  
23 dusting occurred with CrMo steels at temperatures  
24 above 950°F, and stainless steels at temperatures  
25 above 1025°F.

26

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1           Accordingly, another aspect of the invention is  
2   to lower the temperatures of the metal surfaces  
3   inside the furnace tubes, transfer-lines and/or  
4   reactors of the reforming system below the  
5   aforementioned levels. For example, temperatures can  
6   be monitored using thermocouples attached at various  
7   locations in the reactor system. In the case of  
8   furnace tubes, thermocouples can be attached to the  
9   outer walls thereof, preferably at the hottest point  
10   of the furnace (usually near the furnace outlet).  
11   When necessary, adjustments in process operation can  
12   be made to maintain the temperatures at desired  
13   levels.

14

15           There are other techniques for reducing exposure  
16   of system surfaces to undesirably high temperatures  
17   as well. For example, heat transfer areas can be  
18   used with resistant (and usually more costly) tubing  
19   in the final stage where temperatures are usually the  
20   highest.

21

22           In addition, superheated hydrogen can be added  
23   between reactors of the reforming system. Also, a  
24   larger catalyst charge can be used. And, the  
25   catalyst can be regenerated more frequently. In the  
26   case of catalyst regeneration, it is best

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1 accomplished using a moving bed process where the  
2 catalyst is withdrawn from the final bed,  
3 regenerated, and charged to the first bed.  
4

5 Carburization and metal dusting can also be  
6 minimized in the low-sulfur reforming reactor system  
7 of the invention by using certain other novel  
8 equipment configurations and process conditions. For  
9 example, the reactor system can be constructed with  
10 staged heaters and/or tubes. In other words, the  
11 heaters or tubes which are subjected to the most  
12 extreme temperature conditions in the reactor system  
13 can be constructed of materials more resistant to  
14 carburization than materials conventionally used in  
15 the construction of reforming reactor systems;  
16 materials such as those described above. Heaters or  
17 tubes which are not subjected to extreme temperatures  
18 can continue to be constructed of conventional  
19 materials.  
20

21 By using such a staged design in the reactor  
22 system, it is possible to reduce the overall cost of  
23 the system (since carburization resistant materials  
24 are generally more expensive than conventional  
25 materials) while still providing a reactor system  
26 which is sufficiently resistant to carburization and

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1 metal dusting under low-sulfur reforming conditions.  
2 Additionally, this should facilitate the retrofitting  
3 of existing reforming reactor systems to render them  
4 carburization and metal dusting resistant under low-  
5 sulfur operating conditions; since a smaller portion  
6 of the reactor system would need replacement or  
7 modification with a staged design.

8  
9 The reactor system can also be operated using at  
10 least two temperature zones; at least one of higher  
11 and one of lower temperature. This approach is based  
12 on the observation that metal dusting has a  
13 temperature maximum and minimum, above and below  
14 which dusting is minimized. Therefore, by "higher"  
15 temperatures, it is meant that the temperatures are  
16 higher than those conventionally used in reforming  
17 reactor systems and higher than the temperature  
18 maximum for dusting. By "lower" temperatures it is  
19 meant that the temperature is at or about the  
20 temperatures which reforming processes are  
21 conventionally conducted, and falls below that in  
22 which dusting becomes a problem.

23

24 Operation of portions of the reactor system in  
25 different temperature zones should reduce metal  
26 dusting as less of the reactor system is at a



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1 temperature conducive for metal dusting. Also, other  
2 advantages of such a design include improved heat  
3 transfer efficiencies and the ability to reduce  
4 equipment size because of the operation of portions  
5 of the system at higher temperatures. However,  
6 operating portions of the reactor system at levels  
7 below and above that conducive for metal dusting  
8 would only minimize, not completely avoid, the  
9 temperature range at which metal dusting occurs.  
10 This is unavoidable because of temperature  
11 fluctuations which will occur during day to day  
12 operation of the reforming reactor system;  
13 particularly fluctuations during shut-down and start-  
14 up of the system, temperature fluctuations during  
15 cycling, and temperature fluctuations which will  
16 occur as the process fluids are heated in the reactor  
17 system.

18  
19 Another approach to minimizing metal dusting  
20 relates to providing heat to the system using  
21 superheated raw materials (such as e.g., hydrogen),  
22 thereby minimizing the need to heat the hydrocarbons  
23 through furnace walls.

24  
25 Yet another process design approach involves  
26 providing a pre-existing reforming reactor system

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1 with larger tube diameters and/or higher tube  
2 velocities. Using larger tube diameters and/or  
3 higher tube velocities will minimize the exposure of  
4 the heating surfaces in the reactor system to the  
5 hydrocarbons.

6  
7 As noted above, catalytic reforming is well  
8 known in the petroleum industry and involves the  
9 treatment of naphtha fractions to improve octane  
10 rating by the production of aromatics. The more  
11 important hydrocarbon reactions which occur during  
12 the reforming operation include the dehydrogenation  
13 of cyclohexanes to aromatics, dehydroisomerization of  
14 alkylcyclopentanes to aromatics, and  
15 dehydrocyclization of acyclic hydrocarbons to  
16 aromatics. In addition, a number of other reactions  
17 also occur, including the dealkylation of  
18 alkylbenzenes, isomerization of paraffins, and  
19 hydrocracking reactions which produce light gaseous  
20 hydrocarbons, e.g., methane, ethane, propane and  
21 butane, which hydrocracking reactions should be  
22 minimized during reforming as they decrease the yield  
23 of gasoline boiling products and hydrogen. Thus,  
24 "reforming" as used herein refers to the treatment of  
25 a hydrocarbon feed through the use of one or more  
26 aromatics producing reactions in order to provide an

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1 aromatics enriched product (i.e., a product whose  
2 aromatics content is greater than in the feed).  
3

4 While the present invention is directed  
5 primarily to catalytic reforming, it will be useful  
6 generally in the production of aromatic hydrocarbons  
7 from various hydrocarbon feedstocks under conditions  
8 of low sulfur. That is, while catalytic reforming  
9 typically refers to the conversion of naphthas, other  
10 feedstocks can be treated as well to provide an  
11 aromatics enriched product. Therefore, while the  
12 conversion of naphthas is a preferred embodiment, the  
13 present invention can be useful for the conversion or  
14 aromatization of a variety of feedstocks such as  
15 paraffin hydrocarbons, olefin hydrocarbons, acetylene  
16 hydrocarbons, cyclic paraffin hydrocarbons, cyclic  
17 olefin hydrocarbons, and mixtures thereof, and  
18 particularly saturated hydrocarbons.  
19

20 Examples of paraffin hydrocarbons are those  
21 having 6 to 10 carbons such as n-hexane,  
22 methylpentane, n-heptane, methylhexane,  
23 dimethylpentane and n-octane. Examples of acetylene  
24 hydrocarbons are those having 6 to 10 carbon atoms  
25 such as hexyne, heptyne and octyne. Examples of  
26 acyclic paraffin hydrocarbons are those having 6 to

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1 10 carbon atoms such as methylcyclopentane,  
2 cyclohexane, methylcyclohexane and  
3 dimethylcyclohexane. Typical examples of cyclic  
4 olefin hydrocarbons are those having 6 to 10 carbon  
5 atoms such as methylcyclopentene, cyclohexene,  
6 methylcyclohexane, and dimethylcyclohexene.

7  
8 The present invention will also be useful for  
9 reforming under low-sulfur conditions using a variety  
10 of different reforming catalysts. Such catalyst  
11 include, but are not limited to Noble Group VIII  
12 metals on refractory inorganic oxides such as  
13 platinum on alumina, Pt/SN on alumina and Pt/Re on  
14 alumina; Noble Group VIII metals on a zeolite such as  
15 Pt, Pt/SN and Pt/Re on zeolites such as L-zeolites,  
16 ZSM-5, silicalite and beta; and Nobel Group VIII  
17 metals on alkali- and alkaline-earth exchanged L-  
18 zeolites.

19  
20 A preferred embodiment of the invention involves  
21 the use of a large-pore zeolite catalyst including an  
22 alkali or alkaline earth metal and charged with one  
23 or more Group VIII metals. Most preferred is the  
24 embodiment where such a catalyst is used in reforming  
25 a naphtha feed.

26

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1       The term "large-pore zeolite" is indicative  
2       generally of a zeolite having an effective pore  
3       diameter of 6 to 15 Angstroms. Preferable large pore  
4       crystalline zeolites which are useful in the present  
5       invention include the type L zeolite, zeolite X,  
6       zeolite Y and faujasite. These have apparent pore  
7       sizes on the order to 7 to 9 Angstroms. Most  
8       preferably the zeolite is a type L zeolite.

9  
10       The composition of type L zeolite expressed in  
11       terms of mole ratios of oxides, may be represented by  
12       the following formula:



14       In the above formula M represents a cation, n  
15       represents the valence of M, and y may be any value  
16       from 0 to about 9. Zeolite L, its X-ray diffraction  
17       pattern, its properties, and method for its  
18       preparation are described in detail in, for example,  
19       U.S. Patent No. 3,216,789, the contents of which is  
20       hereby incorporated by reference. The actual formula  
21       may vary without changing the crystalline structure.  
22       For example, the mole ratio of silicon to aluminum  
23       (Si/Al) may vary from 1.0 to 3.5.

24  
25       The chemical formula for zeolite Y expressed in  
26       terms of mole ratios of oxides may be written as:

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1  $(0.7-1.1)\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:x\text{SiO}_2:y\text{H}_2\text{O}$

2 In the above formula, x is a value greater than 3 and  
3 up to about 6. y may be a value up to about 9.  
4 Zeolite Y has a characteristic X-ray powder  
5 diffraction pattern which may be employed with the  
6 above formula for identification. Zeolite Y is  
7 described in more detail in U.S. Patent No. 3,130,007  
8 the contents of which is hereby incorporated by  
9 reference.

10

11 Zeolite X is a synthetic crystalline zeolitic  
12 molecular sieve which may be represented by the  
13 formula:

14  $(0.7-1.1)\text{M}_{2/n}\text{O}:\text{Al}_2\text{O}_3:(2.0-3.0)\text{SiO}_2:y\text{H}_2\text{O}$

15 In the above formula, M represents a metal,  
16 particularly alkali and alkaline earth metals, n is  
17 the valence of M, and y may have any value up to  
18 about 8 depending on the identity of M and the degree  
19 of hydration of the crystalline zeolite. Zeolite X,  
20 its X-ray diffraction pattern, its properties, and  
21 method for its preparation are described in detail in  
22 U.S. Patent No. 2,882,244 the contents of which is  
23 hereby incorporated by reference.

24

25 An alkali or alkaline earth metal is preferably  
26 present in the large-pore zeolite. That alkaline

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1 earth metal may be either barium, strontium or  
2 calcium, preferably barium. The alkaline earth metal  
3 can be incorporated into the zeolite by synthesis,  
4 impregnation or ion exchange. Barium is preferred to  
5 the other alkaline earths because it results in a  
6 somewhat less acidic catalyst. Strong acidity is  
7 undesirable in the catalyst because it promotes  
8 cracking, resulting in lower selectivity.

9  
10 In another embodiment, at least part of the  
11 alkali metal can be exchanged with barium using known  
12 techniques for ion exchange of zeolites. This  
13 involves contacting the zeolite with a solution  
14 containing excess  $Ba^{++}$  ions. In this embodiment the  
15 barium should preferably constitute from 0.1% to 35%  
16 by weight of the zeolite.

17  
18 The large-pore zeolitic catalysts used in the  
19 invention are charged with one or more Group VIII  
20 metals, e.g., nickel, ruthenium, rhodium, palladium,  
21 iridium or platinum. The preferred Group VIII metals  
22 are iridium and particularly platinum. These are  
23 more selective with regard to dehydrocyclization and  
24 are also more stable under the dehydrocyclization  
25 reaction conditions than other Group VIII metals. If

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1 used, the preferred weight percentage of platinum in  
2 the catalyst is between 0.1% and 5%.

3

4 Group VIII metals are introduced into large-pore  
5 zeolites by synthesis, impregnation or exchange in an  
6 aqueous solution of appropriate salt. When it is  
7 desired to introduce two Group VIII metals into the  
8 zeolite, the operation may be carried out  
9 simultaneously or sequentially.

10

11 To obtain a more complete understanding of the  
12 present invention, the following examples  
13 illustrating certain aspects of the invention are set  
14 forth. It should be understood, however, that the  
15 invention is not limited in any way to the specific  
16 details set forth therein.

17

18

EXAMPLE 1

19 Tests were run to demonstrate the effect of  
20 sulfur and water on carburization in reforming  
21 reactors.

22

23 In these tests, eight inch long,  $\frac{1}{4}$  inch outside  
24 diameter copper tubes were used as a reactor to study  
25 the carburization and embrittlement of 347 stainless  
26 steel wires. Three of these stainless steel wires



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1 having a diameter of 0.035 inches were inserted into  
2 the tube, while a four inch section of the tube was  
3 maintained at a uniform temperature of 1250°F by a  
4 furnace. The pressure of the system was maintained  
5 at 50 psig. Hexane was introduced into the reactor  
6 at a rate of 25 microliters/min. (1.5 ml/hr) with a  
7 hydrogen rate of about 25 cc/min. (ratio of H<sub>2</sub> to HC  
8 being 5:1). Methane in the product effluent was  
9 measured to determine the existence of exothermic  
10 methane reactions.

11

12 A control run was made using essentially pure  
13 hexane containing less than 0.2 ppm sulfur. The tube  
14 was found to be completely filled with carbon after  
15 only three hours. This not only stopped the flow of  
16 the hydrogen and hexane feeds, the growth of carbon  
17 actually split the tube and produced a bulge in the  
18 reactor. Methane in the product effluent was  
19 approaching 60-80 wt% before plugging.

20

21 Another run was conducted using essentially the  
22 same conditions except that 10 ppm sulfur was added.  
23 The run continued for 50 hours before it was shut  
24 down to examine the wires. No increase in methane  
25 was noted during the run. It remained steady at  
26 about 16 wt% due to thermal cracking. No coke plugs

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1 were found and no carburization of the steel wires  
2 was observed.

3

4 Another identical run was made except that only  
5 1 ppm sulfur was added (10 times lower than the  
6 previous run). This run exhibited little methane  
7 formation or plugging after 48 hours. An examination  
8 of the steel wires showed a small amount of surface  
9 carbon, but no ribbons of carbon.

10

11 Another run was conducted except that 1000 ppm  
12 water (0.1%) was added to the hexane as methanol. No  
13 sulfur was added. The run lasted for 16 hours and no  
14 plugs occurred in the reactor. However, upon  
15 splitting the tube it was discovered that about 50  
16 percent of the tube was filled with carbon. But the  
17 carbon buildup was not nearly as severe as with the  
18 control run.

19

20

#### EXAMPLE 2

21 Tests were conducted to determine suitable  
22 materials for use in low-sulfur reforming reactor  
23 systems; materials which would exhibit better  
24 resistance to carburization than the mild steels  
25 conventionally used in low-sulfur reforming  
26 techniques.

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1           In these tests there was used an apparatus  
2 including a Lindberg alumina tube furnace with  
3 temperatures controlled to within one degree with a  
4 thermocouple placed on the exterior of the tube in  
5 the heated zone. The furnace tube had an internal  
6 diameter of 5/8 inches. Several runs were conducted  
7 at an applied temperature of 1200°F using a  
8 thermocouple suspended within the hot zone (≈2  
9 inches) of the tube. The internal thermocouple  
10 constantly measured temperatures from 0 to 10°F lower  
11 than the external thermocouple.

12  
13           Samples of mild steels (C steel and 2½ Cr) and  
14 samples of 300 series stainless steels were tested at  
15 1100°F, 1150°F and 1200°F for twenty-four hours, and  
16 1100°F for ninety hours, under conditions which  
17 simulate the exposure of the materials under  
18 conditions of low-sulfur reforming. The samples of  
19 various materials were placed in an open quartz boat  
20 within the hot zone of the furnace tube. The boats  
21 were one inch long and ½ inch wide and fit well  
22 within the two-inch hot zone of the tube. The boats  
23 were attached to silica glass rods for each placement  
24 and removal. No internal thermocouple was used when  
25 the boats were placed inside the tube.

26

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1 Prior to start up the tube was flushed with  
2 nitrogen for a few minutes. A carburizing gas of a  
3 commercially bottled mixture of 7% propane in  
4 hydrogen was bubbled through a liter flask of toluene  
5 at room temperature in order entrain about 1% toluene  
6 in the feed gas mix. Gas flows of 25 to 30 cc/min.,  
7 and atmospheric pressure, were maintained in the  
8 apparatus. The samples were brought to operating  
9 temperatures at a rate of 144°F/min.

10

11 After exposing the materials to the carburizing  
12 gas for the desired period at the desired  
13 temperature, the apparatus was quenched with an air  
14 stream applied to the exterior of the tube. When the  
15 apparatus was sufficiently cool, the hydrocarbon gas  
16 was swept out with nitrogen and the boat was removed  
17 for inspection and analysis.

18

19 Prior to start up the test materials were cut to  
20 a size and shape suitable for ready-visual  
21 identification. After any pretreatment, such as  
22 cleaning or roasting, the samples were weighed. Most  
23 samples were less than 300 mg. Typically, each run  
24 was conducted with three to five samples in a boat.  
25 A sample of 347 stainless steel was present with each  
26 run as an internal standard.

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1       After completion of each run the condition of  
2       the boat and each material was carefully noted.  
3       Typically the boat was photographed. Then, each  
4       material was weighed to determine changes while  
5       taking care to keep any coke deposits with the  
6       appropriate substrate material. The samples were  
7       then mounted in an epoxy resin, ground and polished  
8       in preparation for petrographic and scanning electron  
9       microscopy analysis to determine the coking, metal  
10      dusting and carburization responses of each material.

11

12       By necessity, the residence time of the  
13      carburizing gas used in these tests were considerably  
14      higher than in typical commercial operation. Thus,  
15      it is believed that the experimental conditions may  
16      have been more severe than commercial conditions.  
17      Some of the materials which failed in these tests may  
18      actually be commercially reliable. Nevertheless, the  
19      test provides a reliable indication of the relative  
20      resistances of the materials to coking, carburization  
21      and metal dusting.

22

23

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The results are set forth in the Table below.

Table\*

		Wt. % C		
		<u>Gain</u>	<u>Dusting</u>	<u>Composition</u>
1200°F; 24 hours				
C Steel	86	Severe		
2½ Cr	61	Severe		
304	little	No		18 Cr 10 Ni
347	little	No		18 Cr 10 Ni
1150°F; 24 hours				
C Steel	63	Severe		
2½ Cr	80	Severe		
304	1	No		
347	1	No		
1100°F; 24 hours				
C Steel Trace		Trace, localized		
2½ Cr	0	No		
304	0	No		
347	0	No		
1100°F; 90 hours				
C Steel	52	Severe		
2½ Cr	62	Severe		
304	5	No		
347	1	No		

\* 15% C<sub>2</sub>H<sub>6</sub> + 50% C<sub>3</sub>H<sub>8</sub> + H<sub>2</sub> (by weight)

Of course, the above results are qualitative and depend on surface morphology, i.e., microscopic roughness of the metals. The carbon weight gain is indicative of surface coking which is autocatalytic.

EXAMPLE 3

The same techniques used above were used again to screen a wide assortment of materials at a temperature of 1200°F for 16 hours. The results are

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set forth below. Each group represents a side-by-side comparison in a single boat under identical conditions.

TABLE (1)

	<u>Wt. % C</u>	<u>Dusting</u>	<u>Composition</u>
	<u>Gain</u>		
<u>Group I</u>			
Inconel 600	57	Severe	15 Cr 75 Ni
347 oxid. (2)	21	Moderate	
347 Fresh	4	No	18 Cr 10 Ni
<u>Group II</u>			
Inconel 600	40	Severe	15 Cr 75 Ni
310	8	Mild	25 Cr 20 Ni
Incoloy 800	5	Moderate	21 Cr 32 Ni
347	1	Trace	
<u>Group III</u>			
Incoloy 825	<1	Moderate	
Haynes 230	2	Mild	22 Cr 64 Ni
Alonized 347	3	Trace	
347	<1	Trace	
<u>Group IV</u>			
Ni (Pure)	656	Severe	100 Ni
Cu (Pure)	0	No	100 Cu
Sn (Fused)	0	No	
100 Sn			
Tin Can	0	No	
Sn + C Steel			

(1) 15% C<sub>2</sub>H<sub>6</sub> + 50% C<sub>3</sub>H<sub>8</sub> + H<sub>2</sub> (By Wt.)

(2) Roasted in air 2 hours at 1000°C to produce a thin oxide crust.

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EXAMPLE 4

Additional materials were tested, again using the techniques described in Example 2 (unless stated otherwise).

Samples of 446 stainless steel and 347 stainless steel were placed in a sample boat and tested simultaneously in the carburization apparatus at 1100°F for a total of two weeks. The 446 stainless steel had a thin coating of coke, but no other alteration was detected. The 347 stainless steel, on the other hand, had massive localized coke deposits, and pits more than 4 mils deep from which coke and metal dust had erupted.

Samples were tested of a carbon steel screen electroplated with tin, silver, copper and chromium. the samples had coatings of approximately 0.5 mil. After 16-hour carburization screening tests at 1200°F, no coke had formed on the tin-plated and chromium-plated screens. Coke formed on the silver-plated and copper-plated screens, but only where the platings had peeled. Unplated carbon steel screens run simultaneously with the plated screens, exhibited severe coking carburization, and metal dusting.



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1           Samples were tested of a 304 stainless steel  
2           screen; each sample being electroplated with one of  
3           tin, silver, copper and chromium. The samples had  
4           coatings with thicknesses of approximately 0.5 mil.  
5           After 16-hour carburization screening tests at  
6           1200°F, no coke had formed on any of the plated  
7           screens, except locally on the copper-plated screen  
8           where the plating had blistered and peeled. Thin  
9           coke coatings were observed on unplated samples of  
10          304 stainless steel run simultaneously with the  
11          plated screens.

12  
13          Samples were tested of a 304 stainless steel  
14          screen; each sample being electroplated with one of  
15          tin and chromium. These samples were tested along  
16          with a sample of 446 stainless steel in a  
17          carburization test at 1100°F. The samples were  
18          exposed for five weeks. Each week the samples were  
19          cooled to room temperature for observation and  
20          photographic documentation. They were then re-heated  
21          to 1100°F. The tin plated screen was free of coke;  
22          the chromium-plated screen was also free of coke,  
23          except locally where the chrome plate had peeled; and  
24          the piece of 446 stainless steel was uniformly coated  
25          with coke.  
26

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### EXAMPLE 5

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1 insulated cokeballs by diffusion of hydrogen into the  
2 interior catalytic iron dust sites where they  
3 catalyze methane formation from coke and hydrogen.

4  
5 In this experiment steel wool was used to study  
6 methane formation in a micro pilot plant. A  $\frac{1}{4}$  inch  
7 stainless steel tube was packed with 0.14 grams of  
8 steel wool and placed into a furnace at 1175°F.  
9 Hexane and hydrogen were passed over the iron and the  
10 exit stream was analyzed for feed and products. The  
11 steel wool was pretreated in hydrogen for twenty  
12 hours before introduction of the hexane. Then hexane  
13 was introduced into the reactor at a rate of 25  
14 microliters/min. with a hydrogen rate of about 25  
15 cc/min.

16  
17 Initially, methane formation was low, but  
18 continued to increase as the run progressed; finally  
19 reaching 4.5%. Then, 0.1 cc of tetrabutyl tin  
20 dissolved in 2 cc of hexane was injected into the  
21 purified feed stream ahead of the iron. The methane  
22 formation decreased to about 1% and continued to  
23 remain at 1% for the next three hours. The data is  
24 summarized in the Table below.

25  
26

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TABLE

	<u>HOURS</u>	<u>CH4</u>	<u>ETHANE</u>	<u>PROPANE</u>	<u>HEXANE</u>
1					
2					
3					
4					
5	19.2	0.0	0.5	0.3	98.6
6	20.7	1.06	2.08	1.74	93.4
7	21.2	2.62	4.55	3.92	85.3
8	21.5	3.43	4.23	3.83	84.6
9	21.9	4.45	4.50	4.32	82.0
10					
11	22	Tetrabutyl Tin Added			
12					
13	22.6	1.16	3.81	4.12	86.2
14	23.0	1.16	3.96	4.24	85.9
15	23.3	1.0	4.56	3.77	87.5
16	24.3	0.97	3.60	3.76	87.6
17	25.3	1.0	4.47	3.57	88.0
18					
19					

From the results above it can be seen that the addition of tin to the steel wool stops the acceleration of methane formation, and lowers it to acceptable levels in the product.

#### EXAMPLE 6

Additional tests were conducted using tetrabutyl tin pre-coated steel wool. In particular, as in Example 5, three injections of 0.1 cc of tetrabutyl tin dissolved in 2 cc of hexane were injected into a  $\frac{1}{4}$  inch stainless steel tube containing 0.15 grams of steel wool. The solution was carried over the steel wool in a hydrogen stream of 900°F.

The hydrocarbon feed was then introduced at 1175°F at a hydrocarbon rate of 25 microliters/min

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1 with a hydrogen rate of about 25 cc/min. The exit  
2 gas was analyzed for methane and remained below 1%  
3 for 24 hours. The reactor was then shut down, and  
4 the reactor tube was split open and examined. Very  
5 little carburization had occurred on the steel wool.  
6

7 In contrast, a control was run without  
8 tetrabutyl tin pre-treatment. It was run for one day  
9 under the same conditions described above. After 24  
10 hours, no hydrogen or feed could be detected at the  
11 tube exit. The inlet pressure had risen to 300 lbs.  
12 from the original 50 lbs. When the reactor tube was  
13 split open and examined, it was found that coke had  
14 completely plugged the tube.  
15

16 Thus, it can be seen that organo-tin compounds  
17 can prevent carburization of steel wool under  
18 reforming conditions.  
19

#### 20 EXAMPLE 7

21 Another run like the control run of Example 1  
22 was conducted to investigate the effect of  
23 carburization conditions on vapor tin coated  
24 stainless steel wires in a gold plated reactor tube.  
25 The only other difference from the control run was  
26 that a higher hydrogen rate of 100 ml/min was used.

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1           The run continued for eight hours with no  
2           plugging or excessive methane formation. When the  
3           tube was split and analyzed, no plugs or carbon  
4           ribbons were observed. Only one black streak of  
5           carbon appeared on one wire. This was probably due  
6           to an improper coating.

7  
8           This experiment shows that tin can protect  
9           stainless steel from carburization in a manner  
10          similar to sulfur. Unlike sulfur, however, it does  
11          not have to be continuously injected into the feed.  
12          Sulfur must be continuously injected into the feed to  
13          maintain the partial pressure of hydrogen sulfide in  
14          the system at a sufficient level to maintain a  
15          sulfide surface on the steel. Any removal of sulfur  
16          from the feedstock will lead to a start of  
17          carburization after sulfur is stripped from the  
18          reactor system. This usually occurs within 10 hours  
19          after cessation of sulfur.

20  
21          While the invention has been described above in  
22          terms of preferred embodiments, it is to be  
23          understood that variations and modifications may be  
24          used as will be appreciated by those skilled in the  
25          art. For example, portions of steel in the reactor  
26          system can be coated with niobium, zirconium, silica

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1 ceramics, tungsten, or chromium (chromizing),  
2 although these techniques could be excessively  
3 difficult to do or use, or prohibitively expensive.  
4 Or, the use of heat exchangers to heat hydrocarbons  
5 to reaction temperature could be minimized. The heat  
6 could be provided by super-heated hydrogen. Or, the  
7 exposure of heating surfaces to hydrocarbons can be  
8 reduced by using larger tube diameters and higher  
9 tube velocities. Essentially, therefore, there are  
10 many variations and modifications to the above  
11 preferred embodiments which will be readily evident  
12 to those skilled in the art, and which are to be  
13 considered within the scope of the invention as  
14 defined by the following claims.

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WHAT IS CLAIMED IS:

1                   1.    A method for reforming hydrocarbons  
2                   comprising contacting the hydrocarbons with a  
3                   reforming catalyst in a reactor system of improved  
4                   resistance to carburization and metal dusting under  
5                   conditions of low sulfur, and upon reforming said  
6                   resistance being such that embrittlement will be less  
7                   than about 2.5 mm/year.

1                   2.    A method for reforming hydrocarbons  
2                   according to claim 1, wherein said reforming catalyst  
3                   is a large-pore zeolite catalyst including an alkali  
4                   or alkaline earth metal and charged with one or more  
5                   Group VIII metals.

1                   3.    A method for reforming hydrocarbons  
2                   according to claim 2, wherein said hydrocarbons are  
3                   contacted with the catalyst under conditions of low  
4                   water.

1                   4.    A method for reforming hydrocarbons  
2                   according to claim 1, wherein a naphtha feed is  
3                   contacted with a large-pore zeolite catalyst  
4                   including an alkali or alkaline earth metal and  
5                   charged with one or more Group VIII metals, and  
6                   wherein at least a portion of the reactor system has



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7 a resistance to carburization greater than mild steel  
8 under conditions of low sulfur.

1 5. A method for reforming hydrocarbons  
2 according to claim 1, comprising reforming in a  
3 reactor system, at least a portion thereof having a  
4 resistance to carburization greater than mild steel,  
5 under conditions of low sulfur and low water.

1 6. A method for reforming hydrocarbons  
2 according to claim 1, comprising reforming in a  
3 reactor system, at least a portion thereof having a  
4 resistance to carburization greater than aluminized  
5 steels, under conditions of low sulfur and low water.

1 7. A method for reforming hydrocarbons  
2 according to claim 1, comprising reforming in a  
3 reactor system, at least a portion thereof having a  
4 resistance to carburization greater than alloy  
5 steels, under conditions of low sulfur and low water.

1 8. A method for reforming hydrocarbons  
2 according to claim 5, comprising reforming in a  
3 reactor system under conditions of low sulfur, at  
4 least a portion of the reactor system in contact with

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5 the hydrocarbons being comprised of a 300 series  
6 stainless steel.

1 9. A method for reforming hydrocarbons  
2 according to claim 5, comprising reforming in a  
3 reactor system under conditions of low sulfur, at  
4 least a portion of the reactor system in contact with  
5 the hydrocarbons being an alloy containing  
6 substantially no nickel.

1 10. A method for reforming hydrocarbons  
2 according to claim 5, comprising reforming in a  
3 reactor system under conditions of low sulfur, at  
4 least a portion of a furnace tube of the reactor  
5 system in contact with the hydrocarbons having a  
6 resistance to carburization greater than mild steels.

1 11. A method for reforming hydrocarbons  
2 according to claim 5, comprising reforming in a  
3 reactor system under conditions of low sulfur, at  
4 least a portion of a reactor wall of the reactor  
5 system in contact with the hydrocarbons having a  
6 resistance to carburization greater than mild steels.

1 12. A method for reforming hydrocarbons  
2 according to claim 5, comprising reforming in a

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3 reactor system under conditions of low sulfur, at  
4 least a portion of the reactor system in contact with  
5 the hydrocarbons being a material selected from the  
6 group of copper, tin, arsenic, antimony, brass, lead,  
7 bismuth, chromium, intermetallic compounds thereof  
8 and alloys thereof.

1 13. A method for reforming hydrocarbons  
2 according to claim 12, comprising reforming in a  
3 reactor system under conditions of low sulfur, at  
4 least a portion of the reactor system in contact with  
5 the hydrocarbons being a Cu-Sn alloy or a Cu-Sb  
6 alloy.

1 14. A method for reforming hydrocarbons  
2 according to claim 12, wherein said material is  
3 provided as a plating, cladding, paint or other  
4 coating, to a base construction material.

1 15. A method for reforming hydrocarbons  
2 according to claim 12, wherein said material is tin.

1 16. A method for reforming hydrocarbons  
2 according to claim 12, wherein said material is  
3 effective for retaining its resistance to  
4 carburization after oxidation.

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1           17. A method for reforming hydrocarbons  
2           according to claim 1, wherein upon reforming said  
3           resistance is such that embrittlement will be less  
4           than 1.5 mm/year.

1           18. A method for reforming hydrocarbons  
2           according to claim 1, comprising reforming under  
3           conditions of low sulfur and low water.

1           19. A method for reforming hydrocarbons  
2           according to claim 1, comprising contacting the  
3           hydrocarbons with the large-pore zeolite catalyst  
4           under conditions of low sulfur while adding at least  
5           one non-sulfur, anti-carburizing and anti-coking  
6           agent to provide the reactor system of improved  
7           resistance to carburization and metal dusting.

1           20. A method for reforming hydrocarbons  
2           according to claim 19, comprising adding an anti-  
3           carburizing and anti-coking agent selected from the  
4           group of organo-tin compounds, organo-antimony  
5           compounds, organo-bismuth compounds, organo-arsenic  
6           compounds and organo-lead compounds.

1           21. A method for reforming hydrocarbons  
2           according to claim 19, wherein an organo-tin non-

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3 sulfur, anti-carburizing and anti-coking agent is  
4 added.

1 22. A method for reforming hydrocarbons  
2 according to claim 1, wherein at least a portion of  
3 said reactor system is constructed from a chromium  
4 rich steel treated a metal coating comprising tin,  
5 antimony, bismuth or arsenic.

1 23. A method for reforming hydrocarbons  
2 according to claim 1, wherein at least a portion of  
3 the steel surfaces in the reactor system have  
4 initially been coated with aluminum or tin followed  
5 by application of a thin chromium oxide coating.

1 24. A method for reforming hydrocarbons  
2 according to claim 1, wherein at least a portion of  
3 the steel surfaces in said reactor system have  
4 initially been coated with a coating comprising  
5 aluminum, followed by a post-treatment process  
6 comprising application of a metal coating comprising  
7 tin.

1 25. A method for reforming hydrocarbons  
2 according to claim 1, wherein said process at least a  
3 portion of the reactor system is pre-heated with a

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4 hydrogen gas stream heated to a temperature of about  
5 750 to 1150°F, and then said pre-heated portion of  
6 the reactor system is exposed to a cooler gas stream  
7 of about 400 to 800°F which comprises hydrogen and an  
8 organometallic tin compound.

1 26. A method according to claim 1, wherein a  
2 portion of the metal surfaces in the reactor system  
3 has been coated with an aluminum, alumina, chromium  
4 or chromium oxide film, or is constructed of  
5 aluminized or chromized material.

1 27. A method according to claim 1, wherein  
2 the reactor system is at least partially constructed  
3 of a ceramic material.

1 28. A method according to claim 1, wherein  
2 at least a portion of the metal surfaces in the  
3 reactor system is coated with a thin silica or silica  
4 film.

1 29. A method according to claim 1,  
2 comprising maintaining the temperature of the metal  
3 surface of at least a portion of the reactor system  
4 such that it does not exceed a predetermined level,

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5        said level determined such that embrittlement of the  
6        metal surface will be less than 2.5 mm/year.

1                30. A method according to claim 1, wherein  
2        said reactor system staged heaters and/or tubes are  
3        used, or the system has been heated using superheated  
4        raw materials, or larger tube diameters are used, or  
5        higher tube velocities are used, or distinct  
6        temperature zones are used, or a combination thereof,  
7        to an extent effective to provide a resistance such  
8        that embrittlement will be less than 2.5 mm/year.

1                31. A method according to claim 1, wherein  
2        at least a portion of the reactor system is  
3        constructed from mild steels and/or at least a  
4        portion is constructed of stainless steels, wherein  
5        during reforming under conditions of less than 100  
6        ppb sulfur the temperatures of the portions of the  
7        reactor system constructed of mild steels do not  
8        exceed 950°F and the temperatures of the portions of  
9        the reactor system constructed from stainless steels  
10       do not exceed 1025°F.

1                32. The reactor systems used in the methods  
2        of claims 1-31.

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1           33. A decomposable, reactive, tin-containing  
2 paint to be applied to at least a portion of a  
3 reforming reactor system which is exposed to  
4 hydrocarbons at elevated temperatures under  
5 conditions of low sulfur, and provide carburization  
6 resistance such that embrittlement will be less than  
7 2.5mm/year under exposure conditions, which paint  
8 reduces to a reactive tin which forms a tin complex  
9 with said portion of the reforming reactor system to  
10 which it is applied upon heating in a reducing  
11 temperature.

1           34. A decomposable, reactive, tin-containing  
2 paint according to claim 33, said paint comprising  
3 (i) a hydrogen decomposable tin compound, (ii) a  
4 solvent system, (iii) a finely divided tin metal, and  
5 (iv) a tin oxide.

1           35. A decomposable, reactive, tin-containing  
2 paint according to claim 34, wherein said hydrogen  
3 decomposable tin compound is tin octanoate.

1           36. A decomposable, reactive, tin-containing  
2 paint according to claim 34, wherein the finely  
3 divided tin metal has a particle size of about 1 to 5  
4 microns.



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1           37. A decomposable, reactive, tin-containing  
2 paint according to claim 34, wherein the solvent  
3 system contains at least one member selected from  
4 isopropyl alcohol, hexane and pentane.

1           38. A decomposable, reactive, tin-containing  
2 paint according to claim 37, said solvent system  
3 containing isopropyl alcohol.

1           39. A decomposable, reactive, tin-containing  
2 paint according to claim 34, containing no non-  
3 reactive material which will prevent reactive tin  
4 from reacting with the portion of the reforming  
5 reactor system to which the paint is to be applied.

1           40. A decomposable, reactive, tin-containing  
2 paint according to claim 33, applied and reduced.

1           41. A sprayable decomposable, reactive, tin-  
2 containing paint according to claim 33.

1           42. A method for increasing the  
2 carburization resistance of at least a portion of a  
3 reactor system such that embrittlement will be less  
4 than about 2.5mm/year upon exposure to hydrocarbons  
5 at elevated temperatures under conditions of low

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6 sulfur, said method comprising applying a paint  
7 according to claim 33 to at least a portion of the  
8 reactor system and subjecting the applied paint to  
9 reducing conditions.

1 43. A method according to claim 42, said  
2 paint comprising (i) a hydrogen decomposable tin  
3 compound, (ii) a solvent system, (iii) a finely  
4 divided tin metal, and (iv) a tin oxide.

1 44. A paint to be applied to at least a  
2 portion of a reforming reactor system which is  
3 exposed to hydrocarbons at elevated temperatures  
4 under conditions of low sulfur, and provide  
5 carburization resistance such that embrittlement will  
6 be less than 2.5 mm/year under exposure conditions,  
7 said paint comprising:  
8 (i) one or more tin containing compounds,  
9 and  
10 (ii) one or more iron compounds, wherein the  
11 ratio of Fe/Sn is up to 1:3 by weight.

1 45. A paint according to claim 44, wherein  
2 the iron compound is  $\text{Fe}_2\text{O}_3$ .

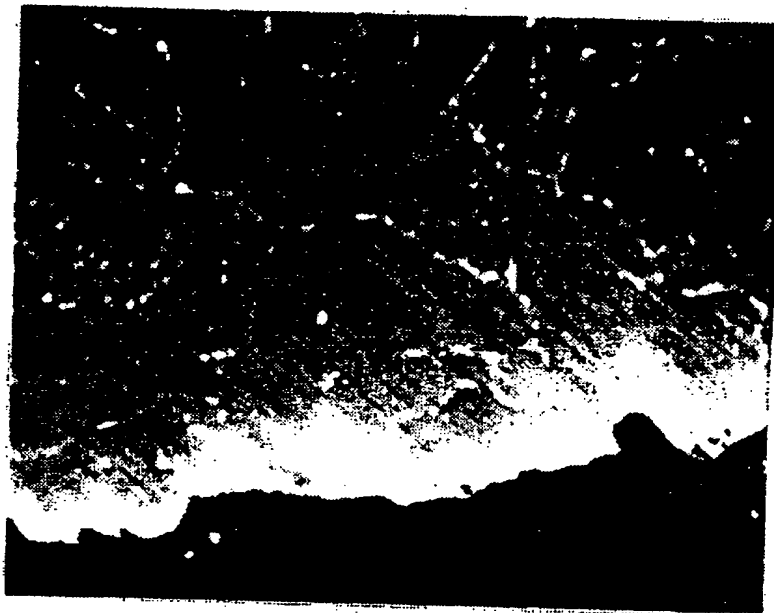
- 89 -

1           46. A paint according to claim 44, said  
2 steel being a mild or stainless steel.

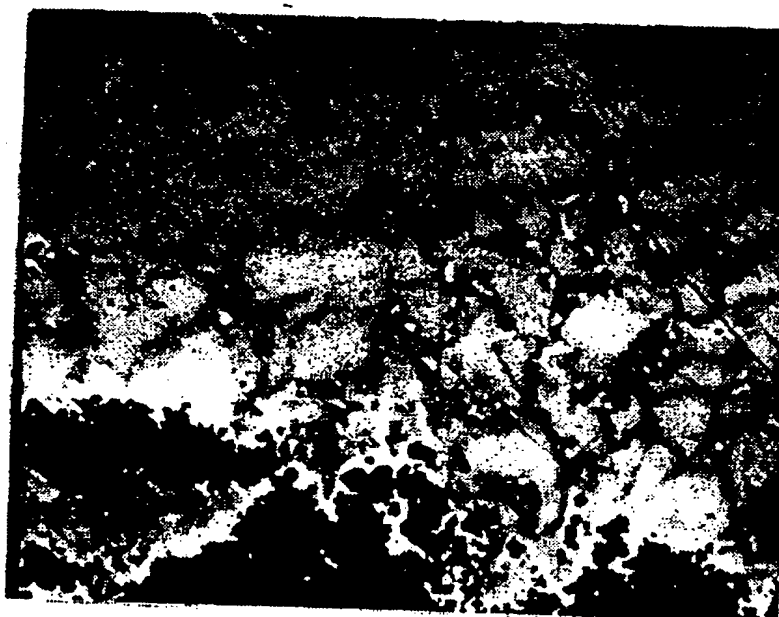
1           47. A method for increasing the  
2 carburization resistance of at least a portion of a  
3 reactor such that embrittlement will be less than  
4 about 2.5 mm/year upon exposure to hydrocarbons at  
5 elevated temperatures under conditions of low sulfur,  
6 said method comprising applying a paint according to  
7 claim 44 to at least a portion of the reactor system.

1           48. A reforming reactor system including  
2 means for providing resistance to carburization and  
3 metal dusting in a method for reforming hydrocarbons  
4 using a large-pore zeolite catalyst including an  
5 alkali or alkaline earth metal and charged with one  
6 or more Group VIII metals under conditions of low  
7 sulfur, said resistance being such that embrittlement  
8 will be less than about 2.5 mm/year, wherein at least  
9 a portion of said reactor system has been coated with  
10 the paint of claim 44.

*Fig. 1A*

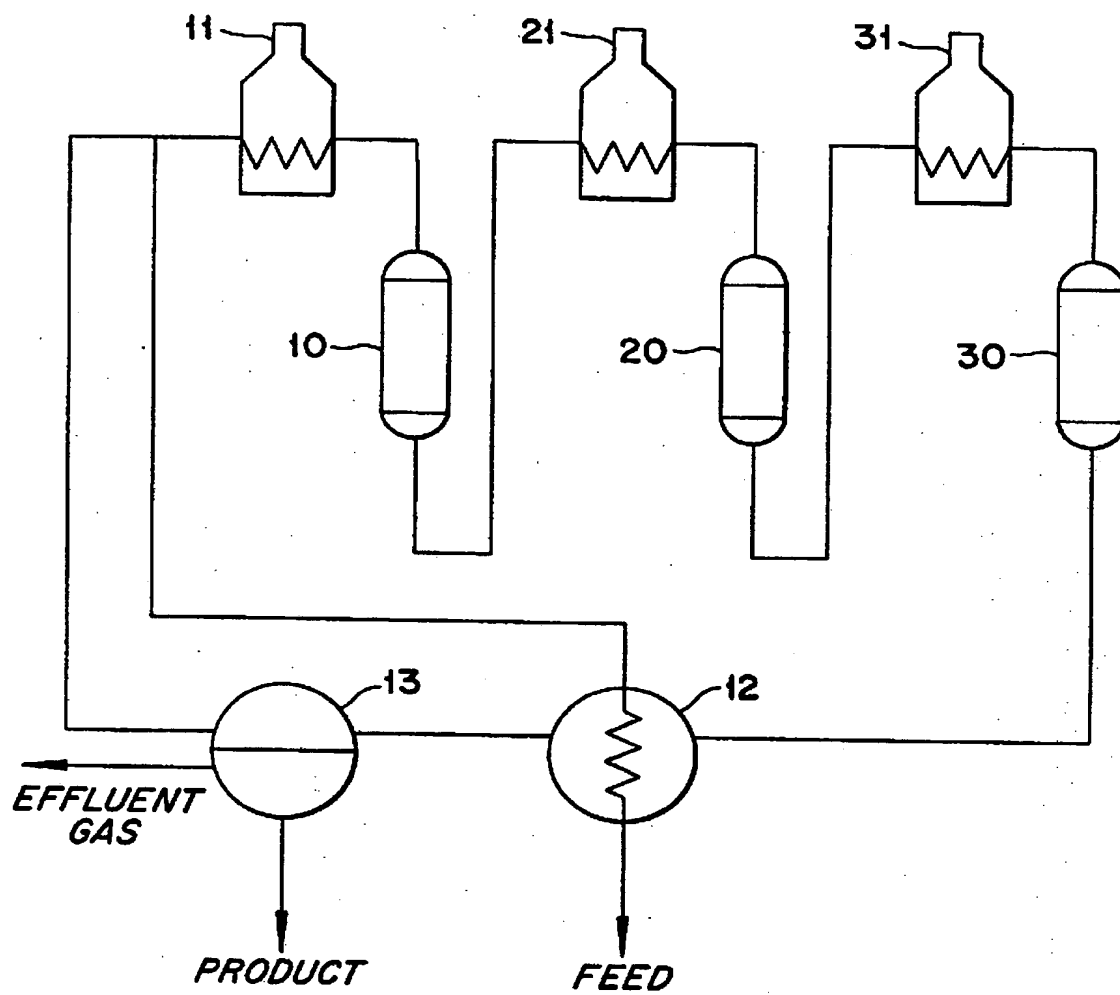


*Fig. 1B*



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*Fig. 2*

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01856

## I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C10G 35/06, 9/16

U.S.Cl.: 208/135

## II. FIELDS SEARCHED

Minimum Documentation Searched \*

Classification System

Classification Symbols

U.S.Cl. 208/137

Documentation Searched other than Minimum Documentation  
to the extent that such Documents are included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, ** with indication where appropriate of the relevant passages **	Relevant to Claim No. :
Y	US, A, 4,456,527 (BUSS ET AL.) 26 June 1984 (See the entire patent).	1-24, 26, 32
Y	US, A, 4,447,316 (BUSS) 08 May 1984 (See the entire patent).	1-24, 26, 32

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- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

14 May 1992

Date of Mailing of this International Search Report

18 JUN 1992

International Searching Authority

ISA/US

Signature of Authorized Officer

Patricia C. Hailey